

United States Patent [19]

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[11] Patent Number: 4,628,136

[45] Date of Patent: Dec. 9, 1986

[54] DEHYDROGENATION PROCESS FOR PRODUCTION OF STYRENE FROM ETHYLBENZENE COMPRISING LOW TEMPERATURE HEAT RECOVERY AND MODIFICATION OF THE ETHYLBENZENE-STEAM FEED THEREWITH

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[21] Appl. No.: 809,913

[22] Filed: Dec. 17, 1985

[51] Int. Cl.⁴ C07C 4/02

[52] U.S. Cl. 585/441; 585/402;

585/440; 585/914

[58] Field of Search 585/402, 440, 441, 914

[56] References Cited

U.S. PATENT DOCUMENTS

3,256,355	6/1966	Gilman et al.	585/914
3,408,263	10/1968	Ward	585/440
3,409,689	11/1968	Ward	585/402
3,515,764	6/1970	Hallman et al.	585/402

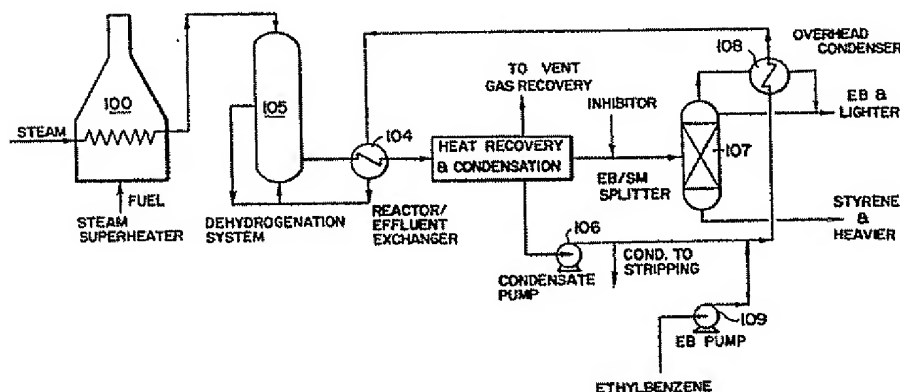
3,690,839 9/1972 Jones 585/402
3,691,020 9/1972 Hughes 585/402

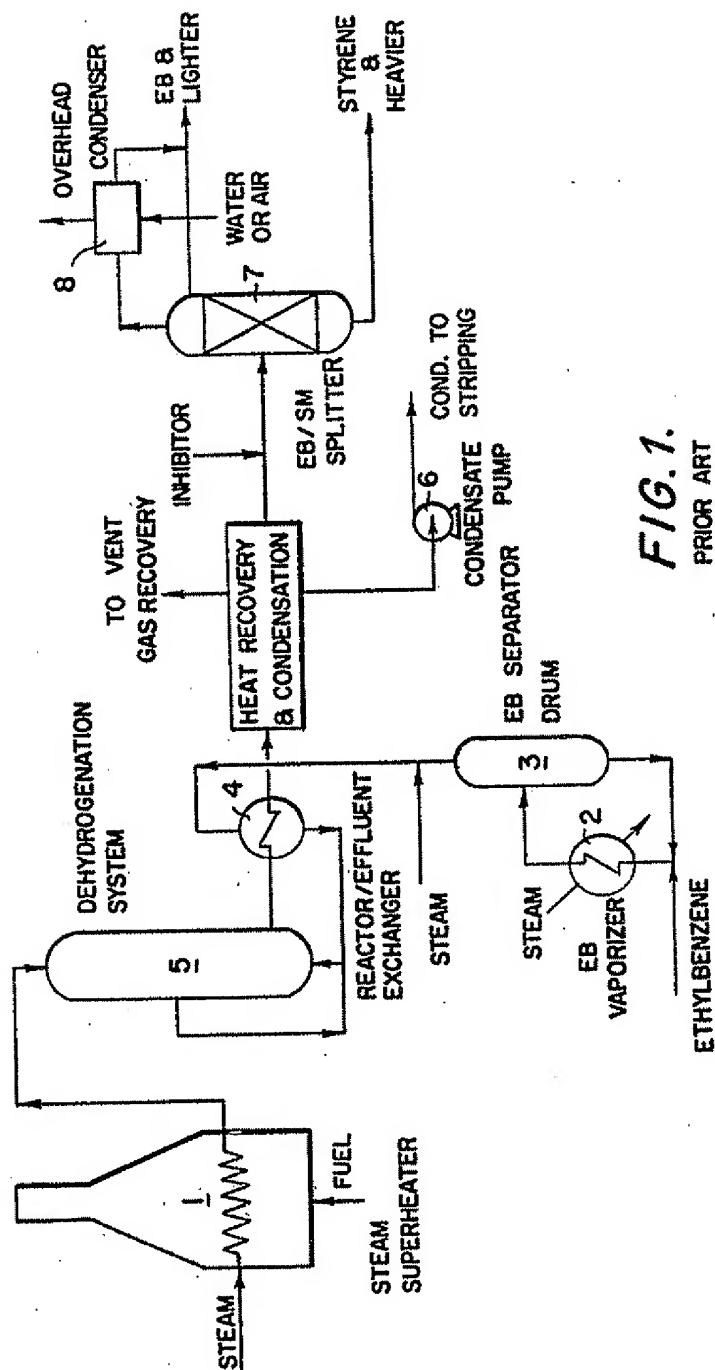
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[57] ABSTRACT

An improved process for the production of styrene through dehydrogenation of ethylbenzene in the presence of steam at elevated temperatures, comprising (1) recovering heat of condensation normally lost during separation of the various components of the dehydrogenation reaction effluent, especially of ethylbenzene from styrene, without need or use of a compressor and (2) using such heat to vaporize an aqueous feed mixture of ethylbenzene and dilution water that is introduced into the dehydrogenation reactor, preferably at about atmospheric pressure, thereby obviating the need to use steam to vaporize the liquid ethylbenzene feed and also enabling much of the diluent steam needed as sensible heat for the dehydrogenation reaction to be generated from water.

11 Claims, 2 Drawing Figures





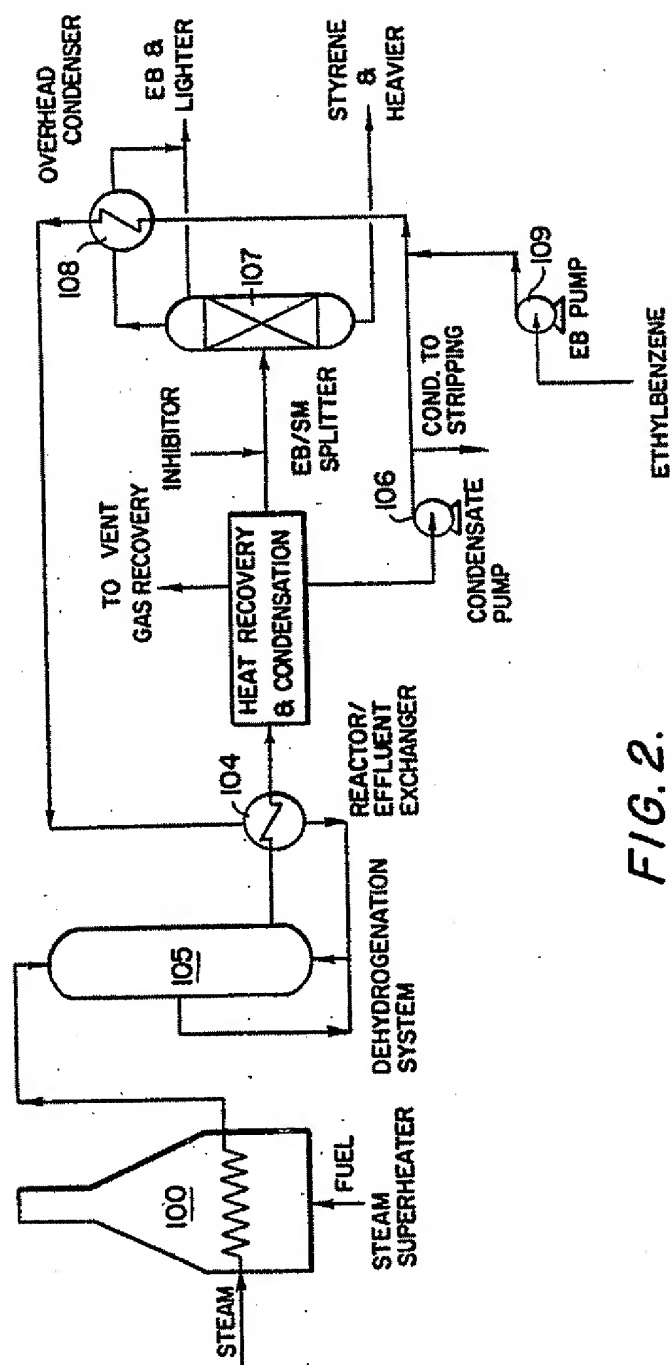


FIG. 2.

DEHYDROGENATION PROCESS FOR PRODUCTION OF STYRENE FROM ETHYLBENZENE COMPRISING LOW TEMPERATURE HEAT RECOVERY AND MODIFICATION OF THE ETHYLBENZENE-STEAM FEED THEREWITH

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for the production of styrene by the dehydrogenation of ethylbenzene in the presence of steam, and more particularly, to a procedure therein for achieving low temperature heat recovery of heat of condensation normally lost during separation of the various dehydrogenation products, most notably of ethylbenzene from styrene, and using such heat to vaporize the liquid ethylbenzene and water feeds to the dehydrogenation reactor without the need or use of a compressor.

2. Description of the Prior Art

It is well known that styrene can be produced from ethylbenzene at temperatures between about 1100 to 1200 degrees F. by vapor phase catalytic dehydrogenation in the presence of steam. Early patents on the subject have concerned themselves essentially with the nature of the catalyst. For example, among the catalysis suggested for this reaction are: palladium oxide catalysts (U.S. Pat. No. 3,502,736); platinum metal catalysts (Japanese Patent Publication No. 8367/67); supported palladium catalysts (Japanese Patent laid-open No. 133236/76); molybdenum-bismuth oxide catalysts (Japanese Patent laid-open No. 52139/76); catalysts containing oxides of at least one metal of copper, zinc, arsenic, antimony, chromium, iron, and/or cobalt (Japanese Patent Publication No. 9168/70); and catalysts containing tin, antimony, and oxygen as essential constituents (British Pat. No. 1,595,008).

More recently, however, the emphasis has shifted from catalyst to means for achieving heat economy in the dehydrogenation process, particularly with regard to the large quantities of diluent steam employed to supply the sensible heat needed for the endothermic reaction in such process and with regard to the separation of styrene from the dehydrogenation reaction effluent products. For example, British Pat. No. 1,122,857 discloses that heat may be transferred from the reactor effluent by using it to generate steam which is thereafter compressed and introduced into the reboiler of the ethylbenzene distillation zone, where styrene is removed by fractionation from ethylbenzene. In this patent, moreover, high pressure steam is used to drive the compressor for the reactor effluent steam generated.

German Offenlegungsschrift No. (OLS) 3,147,323 also focuses on achieving heat economy in the dehydrogenation process. It does so, however, by concentrating on making the dehydrogenation reactor self-sufficient in regard to its steam requirement by recovering the heat, previously abstracted by cooling, for steam generation. Its novelty consists of vaporizing water with a reaction mixture that has been cooled to 90-120 degrees C. and is at a pressure of 0.4-1.2 atm., and compressing the resultant steam to 1.4-2.5 atm. and using it to prepare the ethylbenzene, water, and steam feed mixture. U.S. Pat. No. 3,515,767 embodies the same inventive concept as this Offenlegungsschrift. It teaches the generation of subatmospheric steam from the heat of quenched reaction zone effluent, and compresses the

resulting low pressure steam for use, e.g., as reboiler heat in the product recovery fractionation facilities. However, the improvements of these latter two patent publications require, for their inventive success, a compressor, a heavy duty item of equipment involving substantial investment and expense. The present invention has evolved from the need to avoid these problems and to reduce substantially the energy input and plant investment costs associated with the production of styrene through dehydrogenation of ethylbenzene in the presence of steam at elevated temperatures.

To enable use of the vaporized ethylbenzene-steam mixture in the dehydrogenation process without the need of a compressor, the present invention makes use of novel process improvements. For example, the ethylbenzene-water side of the condenser on the fractionating column separating ethylbenzene and styrene is operated at a pressure adequate for flow through the downstream system. Also, by modifying the ethylbenzene-steam feed system through the mixing of liquid ethylbenzene and water feeds and vaporizing same for introduction, at about atmospheric pressure, into the dehydrogenation reactor, it has been found that the need for steam to vaporize the liquid ethylbenzene feed is eliminated and that much of the diluent steam needed as sensible heat for the dehydrogenation reaction can be generated from liquid water. Other process improvements and simplifications are achieved as well.

SUMMARY OF THE INVENTION

The present invention is thus directed to an improved dehydrogenation process for the production of styrene from ethylbenzene, in the presence of steam, at elevated temperatures through recovering heat of condensation normally lost during separation of the various components of the dehydrogenation reaction effluent, especially of ethylbenzene from styrene, without need or use of a compressor, and using such heat to vaporize an aqueous liquid feed mixture of ethylbenzene (EB) and dilution water that is to be introduced into the dehydrogenation feed reactor, preferably at about atmospheric pressure.

BRIEF DESCRIPTION OF THE DRAWINGS

Understanding of the present invention will be facilitated by reference to the following detailed description, taken in light of the accompanying FIGS. 1 and 2.

FIG. 1 is a simplified schematic flow diagram of the closest prior art dehydrogenation process for the production of styrene from ethylbenzene, in the presence of steam, at elevated temperatures.

FIG. 2 is a simplified, schematic flow diagram of the present invention, which is an improved version of the prior art process shown in FIG. 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE PRESENT INVENTION

The present dehydrogenation process for the production of styrene comprises dehydrogenation of ethylbenzene, preferably in a multi-bed, preferably two-bed, radial flow reactor, using a conventional catalyst for this purpose, such as one based on iron oxide, and conventional operating conditions.

It is understood that certain equipment such as valves, piping, indicators and controls, and the like have been omitted from the drawings to facilitate the descrip-

tion thereof, and that the placement of such equipment at appropriate places is deemed to be within the scope of one skilled in the art.

Referring now to FIG. 1, this represents a typical commercial prior art process for the production of styrene through catalytic dehydrogenation of ethylbenzene (EB), at elevated temperatures approximating 600 degrees C. or more and under low pressure, in the presence of dilution steam.

In FIG. 1, there is depicted, schematically, a steam superheater 1, which is a direct fired heater, for superheating a major portion of the diluent steam (main steam) to a temperature above the dehydrogenation reaction temperature.

Feed ethylbenzene is vaporized in an EB vaporizer 2, which is a conventional thermosiphon reboiler, and passed to an EB separator drum 3. From drum 3, the vaporized EB—diluent steam mixture is mixed with a small portion of the diluent steam and superheated by heat exchange in a heat exchanger 4 with the dehydrogenation reaction effluent. It is then further preheated with the superheated main steam with which it mixes at the reactor inlet of the dehydrogenation reactor 5 before reaction in said reactor 5.

The dehydrogenation reaction effluent, after being heat exchanged in exchanger 4, is passed to the heat recovery and condensation section of the process. Such effluent contains primarily styrene, hydrogen, and unreacted ethylbenzene; small or minor amounts of the dealkylation by-products of benzene and toluene; small or minor amounts of methane, ethane, carbon monoxide, carbon dioxide, polymeric materials, and tars; and also an aqueous condensate. The gaseous phase, which includes some of these materials, and comprises hydrogen, methane, ethane, carbon monoxide, carbon dioxide, benzene, and toluene is recovered by means which include compression and aromatics recovery of the benzene and toluene. The aqueous phase, comprising aqueous condensate, is transmitted by a condensate pump 6, subjected to steam stripping, and reused as boiler feed water. The third and final phase, the organic phase, comprises crude styrene, which has to be distilled in order to recover styrene monomer. Conventionally, the crude styrene, together with a polymerization inhibitor, is fed into a distillation tower 7, which is referred to in the art and known as an ethylbenzene-styrene monomer (EB/SM) "splitter". The polymerization inhibitor, as its name suggests, reduces polymer formation during distillation of the crude styrene. EB/SM splitting can comprise a single distillation tower or a plurality of them ("distillation train"). During distillation, the key separation is that between EB and styrene, and column operation is conducted under reduced pressure conditions so as to reduce temperature and thus styrene polymer. Thus, EB and lighter materials are separated from styrene and heavier materials.

Referring now to FIG. 2, shown there is an improved version of the conventional process depicted in FIG. 1. To facilitate comparison of the two figures, the system of numbering of the respective pieces of process equipment in FIG. 2 parallels that adopted for FIG. 1, except for the use of a "100" series rather than a "1" or single-digit series of numbering. In FIG. 2, there is illustrated a dehydrogenation reactor 105 (designated "dehydrogenation system" as in FIG. 1) into which are passed a main supply of steam, preferably superheated steam, transmitted from direct-fired steam superheater 100, and a feed mixture of ethylbenzene and water, prefera-

bly process steam condensate, said feed mixture being at about atmospheric pressure. The reaction effluent from dehydrogenation reactor 105 is passed into a heat exchanger 104 which transfers heat from the dehydrogenation reaction effluent to the ethylbenzene-water vapor feed mixture, thereby superheating said feed mixture. From exchanger 104 the superheated gaseous feed mixture is passed to dehydrogenation reactor 105. The cooled dehydrogenation reaction effluent from exchanger 104 is passed into additional heat recovery, condensation, and hydrocarbon/steam condensation units in conventional fashion, as indicated by the block denoted "Heat Recovery & Condensation" in both FIGS. 1 and 2. The uncondensed material that remains after such processing, off-gas, comprising non-condensibles (inerts) and uncondensed hydrocarbons and the remaining steam is compressed, scrubbed, and cooled for additional recovery. These measures are denoted by the expression "vent gas recovery" in FIGS. 1 and 2. The liquid water separated during "heat recovery and condensation" is withdrawn by a condensate pump 106, while the hydrocarbons separated from the aqueous phase during such processing, which hydrocarbons comprise unreacted ethylbenzene, styrene, tars, and by-products of benzene and toluene, are then sent to a fractionation column 107, designated as "EB/SM splitter" to denote its primary function. The overhead from the column 107 comprises unreacted ethylbenzene and the by-products benzene and toluene, which are condensed in the overhead condenser 108 into reflux and overhead product. The bottoms from column 107 comprise styrene and tars, which are withdrawn as a bottoms stream. Fresh feed ethylbenzene from pump 109 is mixed with the required diluent steam condensate from condensate pump 106 to form a minimum boiling mixture of ethylbenzene and water which then circulates through the overhead condenser 108. The required quantity of ethylbenzene-water that is fed to reactor 105 vaporizes while condensing the overhead vapor from overhead condenser 108. The net weight ratio of water to ethylbenzene may vary from 0.3 to 0.6, with the preferred ratio being 0.40 to 0.50. The origin of the supply of water is not a critical factor and may be drawn from a variety of sources available in the plant. Most common sources of water would derive from various steam condensates such as process steam condensate or stripped process condensate.

In one of its major, essential aspects, there is provided in this invention an improved method for producing the ethylbenzene-steam feed vapor mixture, thereby conserving considerable amounts of energy and plant investment capital. This method can be employed in all standard conventional commercial styrene processes based upon the dehydrogenation of ethylbenzene in the presence of steam, and it conserves energy whether employed in an adiabatic or an isothermal dehydrogenation process.

To enable use of the vaporized ethylbenzene-steam mixture in the dehydrogenation process without the need for a compressor, the ethylbenzene steam side of the overhead condenser 108 on the fractionating column 107 is operated at a pressure adequate for flow through the downstream system. While not wishing to be limited to specific numerical values, which are variable and dependent on a number of other process factors as is known in the art, nevertheless, for purposes of illustrating this invention, such ethylbenzene steam side pressures of condenser 108 would approximate about 8

to about 25 psi absolute. And the column overhead pressures would approximate about 100 to about 1300 mm mercury, preferably about 100 to 400 mm.

Thus the operating pressure of column 107 is thereby increased from below about 100 mm mercury to give a temperature differential between the condensing ethylbenzene vapor and the vaporizing ethylbenzene-water feed mixture. This differential can be enhanced by the use of a polymerization inhibitor that permits raising of the EB/SM splitter column 107 operating pressure, and thus temperature, without a significant increase in the quantity of styrene polymer produced. Any styrene polymerization inhibitor that meets these requirements would be utilizable in this invention. Thus, examples of suitable polymerization inhibitor would include both sulfur compounds such as sulfur or, more preferably, non-sulfur compounds such as various types of organic compounds, preferably aromatic nitrogen-containing compounds and most preferably aromatic nitro compounds. Representative examples of preferred organic compounds include the following: bis-(2,2,6,6)-tetramethyl piperidyl-1-hydroxylamide adipate; various mixtures of dinitroethyl phenol and dinitrochlorophenol such as 2,6-dinitro-4-ethylphenol and 2,6-dinitro-4-chlorophenol (see U.S. Pat. No. 4,474,646); various mixtures of para-nitrophenol, Mannich base, and paraquinone dioxime (see U.S.S.R. Pat. No. 968,041); tetra 3,5 ditertiary-butyl-4-hydroxybenzyl ethylenediamine; dinitro-phenylhydrazine or diphenyl-carbohydrazide; 4-nitroanthraquinone; 2-methylbenzoquinone-4-oxime; 2,3,5-trimethylbenzoquinone-4-oxime; various mixtures of quinone alkide and a phenol (see U.S. Pat. No. 4,040,911); dinitrophenol (see U.S. Pat. Nos. 3,959,395 and 4,033,829); nitroresol (see U.S. Pat. No. 4,086,147); phenothiazine; t-butyl catechol; nitrosodiphenylamine; and nitrosomethylaniline (see U.S. Pat. No. 4,050,943).

The steam produced in the vaporization of the ethylbenzene-water feed mixture forms part of the diluent steam. Thus, the relative quantity of dilution steam passing through the steam superheater can be reduced with a consequent reduction in the fuel requirements of the superheater. This additional heat input to achieve the same reactor inlet temperature and dilution steam rate is most conveniently taken from the heat recovery system. Thus, the heat normally lost to the operating environment from the distillation column condenser is used to produce steam and ethylbenzene vapor. And hence net steam import is reduced correspondingly. For any given dehydrogenation reactor configuration and operating conditions, plant investment is also reduced since the steam superheater and the distillation column or system become smaller and hence less expensive. In addition, as previously noted, no compressor is needed.

As can be seen, the present invention is not limited to any specific set of process operating conditions or to any specific equipment arrangement. Total dilution steam-ethylbenzene feed ratios, ethylbenzene conversions, dehydrogenation catalyst identities and compositions, and dehydrogenation reactor system configurations can be varied within sundry operable limits without affecting the nature or scope of this invention. Similarly, process details relative to heat recovery and condensation, vent gas recovery, condensate stripping, and the arrangement of the crude styrene distillation column, i.e. EB-SM splitter, are not critical to the success of this invention. Likewise, whether benzene and toluene are separated before or after ethylbenzene and sty-

rene are separated is also a matter not critical to the practice of this invention.

Moreover, this invention offers the same attractive advantages over other methods of producing superheated ethylbenzene or superheated ethylbenzene-steam dehydrogenation reactor feed. For example, ethylbenzene can be vaporized by heat exchange with dehydrogenation reactor effluent, and superheating of the ethylbenzene-steam vapor can be accomplished in the convection section of the steam superheater.

The following table summarizes the typical operating ranges in important dehydrogenation process parameters for styrene processes in which the present invention can be implemented, whether under adiabatic or isothermal conditions.

	Adiabatic	Isothermal
Steam/EB Ratio, wt	1.0-2.2	0.5-1.5
EB Conversion, %	50-90	50-90
Dehydrogenation Temperature, deg. C.	530-650	530-720
Dehydrogenation Pressure, kg/cm ² A	0.3-1.5	0.3-1.5

EXAMPLES OF THE INVENTION

The invention will now be further illustrated by reference to the following specific, non-limiting, comparative example in which two process schemes are compared for a conventional 60,000 metric tons per year styrene plant using benzene and ethylene feedstocks. In one scheme, Scheme A, the present method disclosed and claimed for producing the ethylbenzene-steam vapor feed mixture was absent. In the second scheme, Scheme B, the present method disclosed on page 6, line 24 to page 10, line 19, for producing the ethylbenzene-steam vapor feed mixture was included. The dehydrogenation reaction systems for both schemes were the same, and the recovered vent gas was used as a fuel for the steam superheater. The figures given below for Schemes A and B are based upon 1.0 kilogram of styrene product. All other factors remained constant.

	Scheme A	Scheme B
Steam import, kg	1.729	0.995
Fuel import, kcal	726	614
Cooling water (10 deg. C. min.) kg	113	65
Loss to polymer, kg	0.001	0.0025

The above comparison shows that, in Scheme B, where the present invention was incorporated into the scheme of Process Scheme A, the plant investment cost of Process Scheme A was reduced by 2-3%. It is to be understood, of course, that such savings will vary, depending upon the dehydrogenation system used and upon the economic factors affecting design optimization such as feedstock and utility costs. It is to be further understood that the loss to polymer could be reduced by increasing the rate or amount of feed of the polymerization inhibitor, consistent with the operating limits of the other styrene process parameters.

While the present invention has been described and illustrated with exemplary embodiments, it will be understood that many modifications thereof will be apparent to those of ordinary skill in the art and that this

invention is intended to cover such modifications or any adaptations or variations thereof.

What is claimed is:

1. In a process for the production of styrene from the catalytic dehydrogenation of ethylbenzene in a dehydrogenation zone at elevated temperatures in the presence of steam, whereby the dehydrogenation effluent is cooled and then separated into three phases consisting of a gaseous phase comprising hydrocarbons, an aqueous phase comprising steam condensate, and an organic phase comprising crude styrene and unreacted ethylbenzene, and whereby said crude styrene is separated from said unreacted ethylbenzene by distillation and the styrene monomer product is recovered, the overhead from the distillation column for separating said crude styrene from said unreacted ethylbenzene being passed into a condenser into indirect heat exchange with a fluid comprising ethylbenzene and water passing through said condenser, the improvement comprising operating the ethylbenzene—water side of said condenser at a pressure between about 8 psia and about 25 psia; operating said column under conditions sufficient for its overhead to have a pressure in excess of about 100 mm mercury; said fluid comprising water and ethylbenzene and being vaporized during said indirect heat exchange into a gaseous mixture; and said gaseous mixture being passed into said dehydrogenation zone.

2. A process for the production of styrene according to claim 1, wherein the net weight ratio of water to ethylbenzene in said gaseous mixture is from about 0.3 to about 0.6.

3. A process for the production of styrene according to claim 2, wherein said net weight ratio is about 0.4 to about 0.5.

4. A process for the production of styrene according to claim 2, wherein the pressure of said overhead is above about 100 mm mercury to about 1300 mm mercury.

5. A process for the production of styrene according to claim 1 or 4, wherein the water in said gaseous mixture is derived from steam condensate.

6. A process for the production of styrene according to claim 1, 2, or 4, further comprising a polymerization inhibitor being present during the separation of crude styrene from unreacted ethylbenzene in said column.

7. A process for the production of styrene according to claim 1, wherein the diluent steam/ethylbenzene weight ratio is between 1.0–2.2, the ethylbenzene conversion rate is 50–90%, the temperature in the dehydro-

genation zone ranges from 530–650 degrees C., and the pressure in the dehydrogenation zone ranges from 0.3–1.5 kg/cm²A.

8. A process for the production of styrene according to claim 1, wherein the diluent steam/ethylbenzene weight ratio is between 0.5–1.5, the ethylbenzene conversion rate is 50–90%, the temperature in the dehydrogenation zone ranges from 530–720 degrees C., and the pressure in the dehydrogenation zone ranges from 0.3–1.5 kg/cm²A.

9. A process for the production of styrene according to claim 1, wherein the temperature differential between the condensing ethylbenzene vapor in said condenser and the vaporizing ethylbenzene-water gaseous mixture in said condenser is between about 2 degrees C. and about 10 degrees C.

10. A process for the production of styrene according to claim 6, wherein said polymerization inhibitor is an aromatic nitro compound.

11. In a process for the production of styrene from the catalytic dehydrogenation of ethylbenzene in a dehydrogenation zone at elevated temperatures in the presence of steam, whereby the dehydrogenation effluent is cooled and then separated into three phases consisting of a gaseous phase comprising hydrocarbons, an aqueous phase comprising steam condensate, and an organic phase comprising crude styrene and unreacted ethylbenzene, and whereby said crude styrene is separated from said unreacted ethylbenzene by distillation and the styrene monomer product is recovered, the overhead from the distillation column for separating said crude styrene from said unreacted ethylbenzene being passed into a condenser into indirect heat exchange with a fluid passing through said condenser, the improvement comprising operating the ethylbenzene steam side of said condenser at a pressure between about 8 psia and about 25 psia; operating said column under conditions sufficient for its overhead to have a pressure in excess of about 100 mm mercury—about 1300 mm mercury; said fluid comprising water and ethylbenzene and being vaporized during said indirect heat exchange into a gaseous mixture; said gaseous mixture being passed into said dehydrogenation zone; the net weight ratio of water to ethylbenzene in said gaseous mixture being from about 0.3–about 0.6; and a polymerization inhibitor being present during the separation of crude styrene from unreacted ethylbenzene in said column.

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United States Patent [19]

Faure et al.

[11] Patent Number: 4,774,378

[45] Date of Patent: Sep. 27, 1988

[54] PROCESS FOR PRODUCTION OF STYRENE

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[21] Appl. No.: 29,105

[22] Filed: Mar. 23, 1987

[30] Foreign Application Priority Data

Mar. 21, 1986 [FR] France 86 04066

[51] Int. Cl.⁴ C07C 4/02

[52] U.S. Cl. 585/441

[58] Field of Search 585/441

[56] References Cited

U.S. PATENT DOCUMENTS

3,660,510 5/1972 Kindler et al. 585/441

4,113,787 9/1978 Ward 585/441

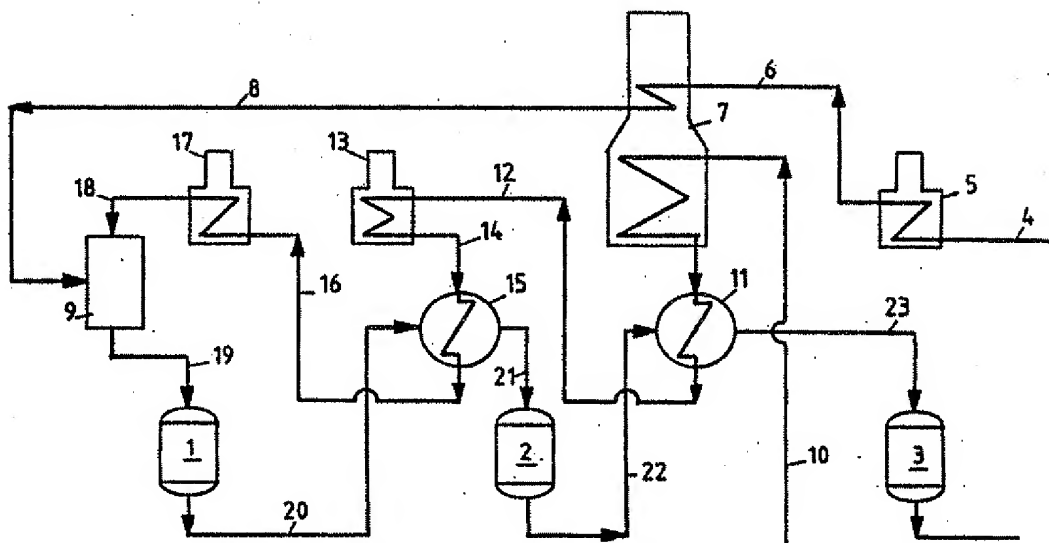
4,347,396 8/1982 Takano et al. 585/441

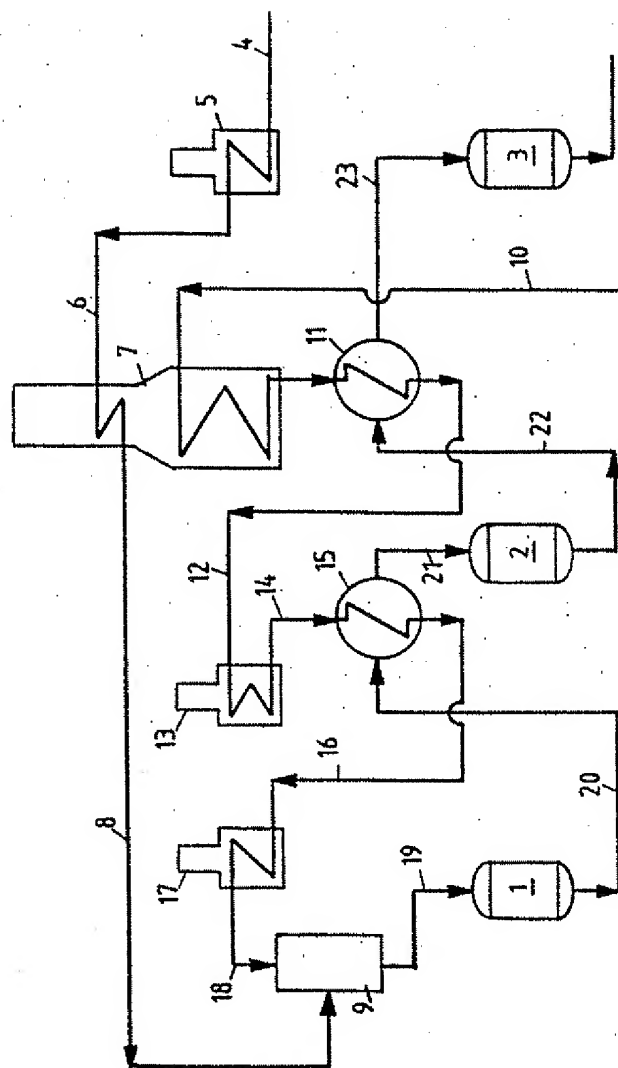
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[57] ABSTRACT

The present invention relates to a process for the production of styrene by the catalytic dehydrogenation of ethylbenzene into styrene in the presence of steam which is, in a first stage, used for heating the reaction effluents, and then used as diluent for ethylbenzene. This process is characterized in that: a molar ratio of steam:ethylbenzene of between 5 and 13 is used, the temperature in the dehydrogenation reactors is between 580° and 645° C., the average pressure in the first reactor is 0.6–1 kg/cm² and those in the second and the third reactors is 0.4–0.7 kg/cm², and the hourly space velocity of liquid ethylbenzene is 0.20–0.35 h⁻¹.

12 Claims, 1 Drawing Sheet





- FIGURE 1 -

PROCESS FOR PRODUCTION OF STYRENE

BACKGROUND OF THE INVENTION

The present invention relates to a new process for producing styrene by the catalytic dehydrogenation of ethylbenzene into styrene in the presence of steam.

Styrene is widely used as raw material for the production of a large number of resins, plastics and elastomers, the extent of its use being mainly attributed to the suitability of styrene to be easily polymerized, for example, into polystyrene, or to be copolymerized, for example with butadiene, to produce rubbers.

The production of styrene, as regards the dehydrogenation process as well as the variety of catalysts used in this process, is well known. As present, the main research objective lies in the improvement of the profitability of the process. Especially, a process for the dehydrogenation of ethylbenzene according to which the dehydrogenation is carried out in a plant which comprises at least three dehydrogenation reactors in series, and intermediate heating devices for the reactors in which the reaction effluents are subjected to a heating by heat exchange with steam is known. According to this process, steam is first of all used for heating the reaction effluents and it is then mixed with ethylbenzene at the inlet of the first reactor. The operating conditions adopted in this process are the mixing of 3 to 10 moles of steam with 1 mole of ethylbenzene, and a temperature and a pressure at the inlet of the last reactor of 600°-680° C. and 0.4-0.8 kg/cm², respectively. The temperature and pressure conditions at the inlet of the other reactors are 600°-680° C. and 2-0.4 kg/cm² (absolute), respectively, and the overall space velocity of ethylbenzene is equal to or greater than 0.44 h⁻¹. By hourly space velocity of ethylbenzene is meant the ratio of the volume flowrate of ethylbenzene to the total volume of the catalyst. According to this process, an ethylbenzene conversion rate of the order of 65-75%, or even greater, and a molar selectivity of the order of 90% are obtained. However, the implementation of such a process, over a period of time, leads to a deterioration in the styrene selectivity as well as in the ethylbenzene conversion rate which may, nevertheless, be limited by increasing the reaction temperatures. In fact, gradual degradation of the catalyst and appearance of carbon deposits on this catalyst are observed over a period of time. Additionally, the presence of hot points along the production line (especially in the intermediate heating devices) gives rise to thermal degradation reactions producing heavy and choking compounds. It is estimated that the rate of heavy products formed is of the order of 17000 ppm, expressed per ton of effluent hydrocarbons, or even greater. In the end, an increase in charge loss, a decrease in the efficiency of the catalyst and, therefore, the need for frequent cleaning, results therefrom. With a view to eliminating the drawbacks of such a process, the Applicant Company has developed a new process for the dehydrogenation of ethylbenzene which makes it possible to obtain excellent ethylbenzene conversion rates, greater than 73%, and a molar selectivity greater than 93%.

SUMMARY OF THE INVENTION

More precisely, the subject of the invention is a process for producing styrene by the catalyst dehydrogenation of ethylbenzene according to which the dehydrogenation is carried out in a plant which comprises three

dehydrogenation reactors in series, one or more heating devices arranged between the reactors in which the reaction effluents are subjected to a heating by heat exchange with steam, which is used, in a first stage, to heat the reaction effluents, and which is mixed, in a second stage, with the ethylbenzene at the inlet of the first dehydrogenation reactor. The process according to the invention is characterized in that:

ethylbenzene is mixed with steam in a molar ratio of steam:ethylbenzene of between 5:1 and 13:1, the mixture is heated at the inlet of the said reactors to a temperature of between 580° and 645° C., an average pressure in the first reactor of between 0.6 and 1.0 kg/cm², expressed as absolute pressure, and a pressure of between 0.40 and 0.70 kg/cm², expressed as absolute pressure, in the second and the third reactors are maintained, and an overall space velocity of liquid ethylbenzene of between 0.20 and 0.35 h⁻¹ is imposed.

According to a preferred embodiment of the process according to the invention an overall space velocity of liquid ethylbenzene of between 0.24 and 0.30 h⁻¹ is imposed.

Preferably, the temperature at the inlet of the reactors is maintained between 595° and 630° C.

Preferably still, the average pressure in the first reactor is between 0.6 and 0.8 kg/cm², expressed as absolute pressure, the average pressure in the second reactor is between 0.5 and 0.7 kg/cm², expressed as absolute pressure or the average pressure, in the third reactor is between 0.4 and 0.6 kg/cm², expressed as absolute pressure.

Preferably still, a molar ratio of steam:ethylbenzene of between 7:1 and 13:1 is imposed, the conversion of ethylbenzene and the molar selectivity being higher in this range.

The process according to the invention may be used with conventional catalysts used for the dehydrogenation of ethylbenzene. Catalysts based on iron oxide and, in particular, those which contain potassium, may especially be mentioned.

Any ethylbenzene dehydrogenation reactor may be employed for implementing the process according to the invention. However, radial reactors of the type described in French Patent No. 2,365,370 are preferably used.

In accordance with the process according to the invention, which is carried out under moderate conditions of temperature and at low pressure and low overall space velocity of the liquid ethylbenzene, a significant restriction is achieved in the formation of heavy degradation products. In fact, in accordance with the process according to the invention, the rate of heavy products formed does not exceed 5000 ppm per tonne of effluent hydrocarbons.

In accordance with the process according to the invention, ethylbenzene conversion rates which may reach 75% or higher, and a selectivity of the order of 95% or even greater, are obtained.

Moreover, the decrease in the formation of heavy and choking degradation products enables this performance to be maintained over a period of time and avoids the frequent stoppages of the plants for cleaning.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be better understood on reading the practical embodiments of the present invention,

given by way of indication and without implied limitation, and carried out using the styrene manufacturing plant described below and shown in FIG. 1.

According to the invention, the plant shown in FIG. 1 comprises three dehydrogenation reactors 1, 2 and 3, arranged in series.

DETAILED DESCRIPTION OF THE DRAWINGS

Ethylbenzene is first of all vaporized in an exchanger (not shown in FIG. 1) and then introduced through the circuit 4 into a furnace 5 and then through the circuit 6 into the furnace 7. The ethylbenzene is then brought through the circuit 8 into the mixer 9 to be mixed therein with steam.

Water, which has previously been vapourized in a boiler (not shown in FIG. 1), is brought through the circuit 10 into the furnace 7. The steam then undergoes a series of heat exchanges, thus playing the role of a high-temperature heat exchange fluid:

at the outlet of the furnace 7, the steam is brought into the indirect heat exchanger 11 to heat the effluents originating from the reactor 2,

the steam is then brought through the circuit 12 into the furnace 13 to be heated therein,

the steam is then introduced through the circuit 14 into the indirect heat exchanger 15 to heat the effluents from the reactor 1,

the steam is then introduced through the circuit 16 into the furnace 17 to be reheated therein, and the steam is then injected through the circuit 18 into the mixer 9 to be mixed with ethylbenzene therein.

As it leaves the mixer 9, the ethylbenzene-steam reaction mixture, the steam:ethylbenzene molar ratio of which is, according to the invention, between 5 and 13, has a temperature of the order of 580°-645° C.

The reaction mixture thus obtained is injected through the circuit 19 into the reactor 1 in which it passes through the first catalytic bed. The pressure at the boundaries of this reactor must be adjusted so as to have an average pressure, expressed as absolute pressure, of 0.6-1 kg/cm² and preferably of 0.6 to 0.8

tively. On exit from the exchanger 15, the reaction mixture has a temperature sufficient to undergo a dehydrogenation once again, at a temperature of between 580° and 645° C. The effluent is therefore directed through the circuit 21 into the reactor 2 in which it passes through the second catalytic bed. The pressure at the boundaries of this reactor must be adjusted so as to have an average pressure, expressed as absolute pressure, preferably of 0.5-0.7 kg/cm², and preferably still, of 0.52-0.65 kg/cm². On exit from this reactor, the effluent is brought through the circuit 22 into the heat exchanger 11 for heating and then through the circuit 23 into the reactor 3 in which it passes through the third catalytic bed. The pressure at the boundaries of this reactor must be adjusted so as to have an average pressure, expressed as absolute pressure, preferably of 0.4-0.6 kg/cm², and preferably still, of 0.4-0.5 kg/cm².

On exit from the reaction zone, the effluent is first of all directed into devices for energy recovery (not shown in FIG. 1) and is then directed towards the styrene purification phase.

The space velocity of liquid ethylbenzene in the reactors 1, 2 and 3 is adjusted so as to have an overall space velocity of between 0.20 and 0.35 h⁻¹ and preferably between 0.24 and 0.30 h⁻¹.

EXAMPLES

Examples of practical implementation Nos. 1, 2, 3, 4 and 5 and comparative examples 6 and 7.

The catalytic dehydrogenation of the ethylbenzenes-steam mixture was carried out using a plant, the block diagram for the production of which is shown in FIG. 1. The reaction conditions for the dehydrogenation and the results are given in table 1. Example Nos. 1, 2, 3, 4 and 5 relate to the implementation of the dehydrogenation process according to the invention whereas the comparative examples 6 and 7 correspond to the implementation of the conventional dehydrogenation process, the operating conditions of which are mentioned in the first part of our application.

In addition, the catalyst used in the examples is based on iron oxide and contains especially potassium.

TABLE No. 1

	EXAMPLES					COMPARATIVE EXAMPLES	
	N° 1	N° 2	N° 3	N° 4	N° 5	N° 6	N° 7
Molar ratio of steam:ethylbenzene	12.4	9.4	8.20	7	5.3	6	4
Temp. (in °C.) at the inlet of the							
1st reactor	620	625	620	595	600	650	650
2nd reactor	620	625	620	600	600	650	650
3rd reactor	620	625	620	600	600	650	650
Overall space velocity (in h ⁻¹)	0.24	0.27	0.30	0.25	0.27	0.44	0.44
Average pressure (in kg/cm ²)							
1st reactor	0.84	0.76	0.75	0.72	0.71	0.90	0.86
2nd reactor	0.64	0.60	0.58	0.59	0.57	0.81	0.80
3rd reactor	0.50	0.47	0.45	0.47	0.47	0.68	0.68
Conversion of ethylbenzene	80	73	73.3	64.7	56.6	72.1	66.7
Selectivity (in mole %)	95.8	94.9	93.6	93.4	94.5	90.9	89.8
Heavies formed (in ppm)	1200	2400	4000	900-1000	2000	16800	18000

kg/cm². On exit from the reactor 1, the reaction mixture or effluent is directed through the circuit 20 into the heat exchanger 15 for heating. Because of the endothermic nature of the dehydrogenation reaction, the mixture undergoes a temperature drop of a few tens of degrees in the dehydrogenation reactors 1, 2 and 3. Advantageously and in accordance with the invention, the reaction effluents are heated in the heat exchangers 15 and 11 before being injected into the reactors 2 and 3 respec-

We claim:

1. A process for producing styrene by catalytic dehydrogenation of ethylbenzene wherein the dehydrogenation is conducted in three separate dehydrogenation zones in series, one or more heating means arranged between said zones wherein reaction effluents are heated by indirect heat exchange with steam which

after being used to heat said reaction effluents, is mixed with the ethylbenzene at the inlet of the first dehydrogenation reaction zone and wherein:

the ethylbenzene is mixed with the steam in a molar ratio, steam: ethylbenzene, of between 5:1 and 13:1, the resultant mixture is heated at the inlet of the reaction zones to a temperature of between 580° and 645° C.,

an average pressure in the first reaction zone of between 0.6 and 1 kg/cm², expressed as absolute pressure, and a pressure of between 0.40 and 0.70 kg/cm², expressed as absolute pressure, in the second and the third reaction zones are maintained, and

an overall space velocity of the liquid ethylbenzene therein of between 0.20 and 0.35 h⁻¹ is imposed.

2. Process according to claim 1, wherein the overall space velocity of the liquid ethylbenzene is between 0.24 and 0.30 h⁻¹.

3. Process according to claim 1 or 2, wherein the temperature at the inlet of the reactors is maintained between 595° and 630° C.

4. Process according to claim 1, wherein the average pressure in the first reaction zone is between 0.6 and 0.8 kg/cm², expressed as absolute pressure.

5. Process according to claim 1, wherein the average pressure in the second reaction zone is between 0.5 and 0.7 kg/cm², expressed as absolute pressure.

6. Process according to claim 1, wherein the average pressure in the second reaction zone is between 0.52 and 0.65 kg/cm², expressed as absolute pressure.

7. Process according to claim 1, wherein the average pressure in the third reaction zone is between 0.4 and 0.6 kg/cm², expressed as absolute pressure.

8. Process according to claim 1, wherein the average pressure in the third reaction zone is between 0.4 and 0.5 kg/cm², expressed as absolute pressure.

9. Process according to claim 1, wherein the overall space velocity of the liquid ethylbenzene is between 0.24 and 0.30 h⁻¹, wherein the temperature at the inlet of the reaction zone is maintained between 595° and 630° C., wherein the average pressure in the first reaction zone is between 0.6 and 0.8 kg/cm², wherein the average pressure in the second reaction zone is between 0.5 and 0.7 kg/cm², and wherein the average pressure in the third reaction zone is between 0.4 and 0.6 kg/cm², expressed as absolute pressure.

10. A process according to claim 1, wherein the steam:ethylbenzene molar ratio is between 7:1 and 13:1.

11. A process according to claim 9, wherein the steam:ethylbenzene molar ratio is between 7:1 and 13:1.

12. A process according to claim 1, wherein the rate of heavy products formed does not exceed 5000 ppm per ton of effluent hydrocarbon

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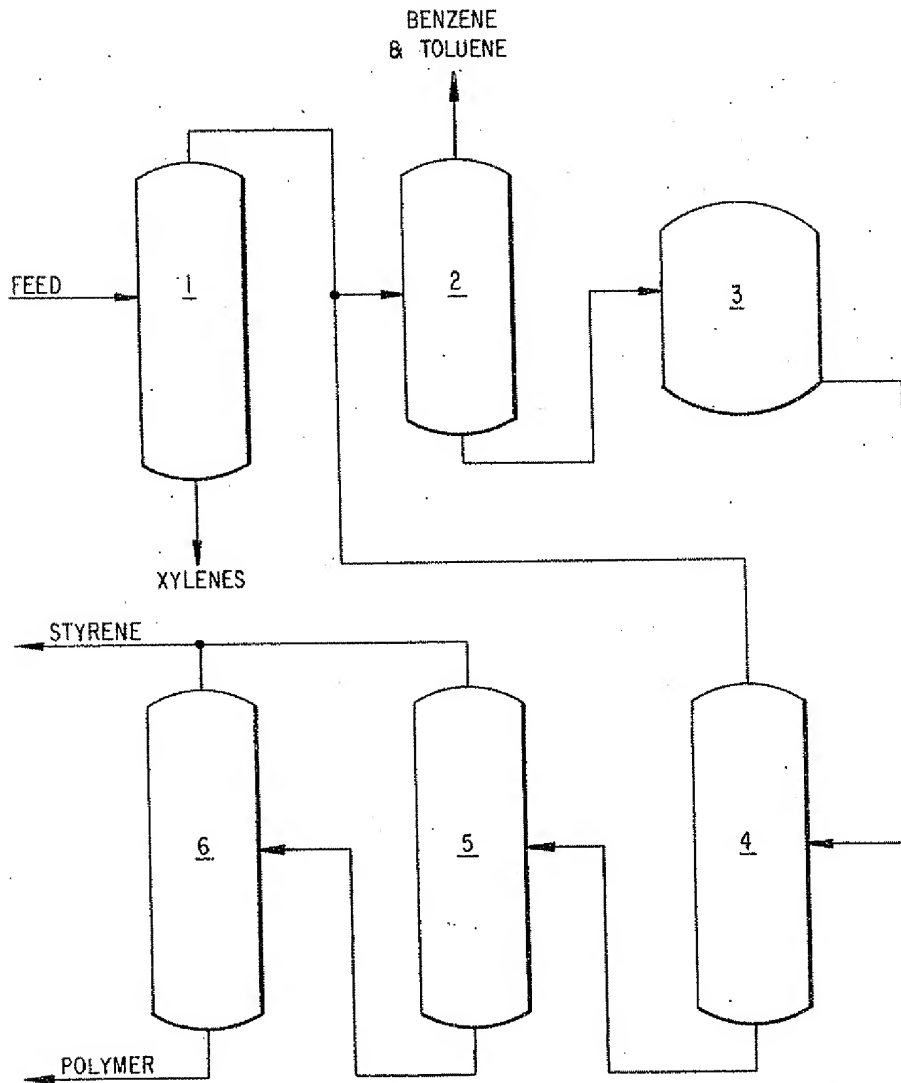
March 7, 1967

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3,308,179

PROCESS FOR DEHYDROGENATION OF ETHYLBENZENE

Filed Jan. 31, 1964



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1

3,308,179 PROCESS FOR DEHYDROGENATION OF ETHYLBENZENE

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Filed Jan. 31, 1964, Ser. No. 341,535
7 Claims. (Cl. 260-669)

This invention relates to the production of high purity styrene by dehydrogenation in a system into which is fed a relatively impure ethylbenzene stream. According to the process of this invention, high purity styrene, for instance, having a purity of at least 99 weight percent or even at least 99.5%, based on C_8 aromatic hydrocarbons is produced in a catalytic dehydrogenation process using an ethylbenzene feedstock of a purity of 95 to 98.5 weight percent, preferably 96 to 97.5%.

The catalytic dehydrogenation of ethylbenzene to form styrene is well known in the art. For polymerization grade styrene, a purity of at least 99.5% is usually required. Styrene containing more than about 1% of a stable hydrocarbon boiling in the C_8 aromatics range is generally useless for normal commercial polymer purposes. Thus in the production of commercial styrene, it is very important to prevent the presence of impurities in the product. Normally the styrene-containing effluent which has been formed by dehydrogenation of feeds prepared by separation from petroleum fractions, contains both ethylbenzene as a result of incomplete dehydrogenation and xylene impurities. The ethylbenzene and xylene are normally removed overhead from the styrene product bottoms and the overhead is recycled to the dehydrogenation reactor. Thus it was considered that the making of a styrene product of given concentration permitted the presence of xylene in the feed only to the same extent since any xylene in the ethylbenzene feed would build up in the recycle stream until equilibrium is established and at this point, the amount of xylene which goes into the styrene product is equal to the amount of xylene entering as an impurity in the ethylbenzene feed. Therefore it has been considered necessary to use an ethylbenzene feed of extremely high purity, normally greater than 99.5%. See U.S. Patents Nos. 2,959,626 and 3,084,108.

The object of this invention is to prepare high purity styrene using as a starting material ethylbenzene of relatively lower purity. The object of this invention is further to make it possible to produce high purity styrene by the use of less expensive ethylbenzene feed distillation systems than heretofore required or to increase the capacity of existing systems for obtaining the ethylbenzene feed stream from aromatic petroleum fractions. For example, the amount of ethylbenzene available for dehydrogenation, and thus the amount of styrene produced may be increased by about 21% when the ethylbenzene fed to the dehydrogenation system is only 97% pure, rather than 99.5%, based on total C_8 hydrocarbons.

The process of this invention is based upon the discovery that in the system of the present invention sufficient amounts of xylenes are cracked in the dehydrogenation reactor to lower boiling impurities such as benzene and toluene. As a practical matter, all xylenes are not removed from the styrene product. Thus the amount of xylenes cracked plus the amount of xylene in the styrene product is essentially equal to the amount of xylene entering in the ethylbenzene feed, and accordingly the amount of xylenes cracked is essentially equal to the amount of xylene in the C_8 aromatic hydrocarbon feed stream minus the xylene in the styrene product.

In the process for purification of the ethylbenzene feedstock, two distillation columns are often employed. The

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first separates the bulk of the higher boiling xylenes from ethylbenzene and the second removes the lower boiling benzene and toluene from the ethylbenzene. This sequence can be reversed; however, by removing the benzene and toluene first. A common column may be employed for distilling benzene and toluene from the feedstock and from the C_8 stream being recycled in the dehydrogenation system. In any event, according to this invention, the ethylbenzene feed to the dehydrogenation system contains 95 to 98.5%, preferably 96 to 97.5%, ethylbenzene based on the total of ethylbenzene and xylenes.

After separation, the ethylbenzene is catalytically dehydrogenated. Generally the dehydrogenation temperature should be in the range of about 1000 to 1200° F. and preferably about 1050 to 1175° F. Any suitable ethylbenzene dehydrogenation catalyst may be used. Typical dehydrogenation catalysts are commercially available catalysts which comprise 90% Fe_2O_3 , 4% Cr_2O_3 and 6% K_2CO_3 ; or 62.5% Fe_2O_3 , 2.2% Cr_2O_3 and 35.3% K_2CO_3 . Other suitable catalyst compositions are as follows: 60-95% iron oxide, 4-39% potassium oxide and 1-10% chromium oxide; 5-60% cobalt oxide, 10-60% iron oxide, 4-39% potassium oxide and 1-10% chromium oxide and 50-90% iron oxide, 9-49% calcium oxide and 1-4% chromium oxide. These catalysts often consist essentially of the oxides of an iron group metal; an alkaline metal including the alkali and alkaline earth metals and chromium. The oxide form of the metals includes compounds that decompose to an oxide under the reaction or similar conditions.

The dehydrogenation may be carried out at atmospheric or elevated or reduced pressures. With pressures in the range of about 200 p.s.i.g. the hydrocarbon feed is often diluted with from about 1 to 10 volumes of steam to reduce the hydrocarbon partial pressure. The space velocity can be varied and when using a catalyst the WHSV (pounds hydrocarbon per pound of catalyst per hour) may often vary from about 0.1 to 5, preferably from 0.4 to 0.7. In general, standard dehydrogenation reactor conditions have been found satisfactory.

It has been found that the amount of xylenes cracked increases with increasing ethylbenzene conversion, and it is usually only necessary to keep the conversion of ethylbenzene high enough so that the amount of xylene cracked is about equal to the amount in the feed minus that in the styrene product. In general, the ethylbenzene conversion will be in the range of about 25 to 70%, preferably about 30 to 60%. It is desirable that the distillation column for separating the recycle stream be capable of separating xylene and ethylbenzene from styrene without a large amount of styrene going to the recycle stream in order to avoid undue polymerization of the styrene in the dehydrogenation reactor. Generally, the column should be capable of making a separation which yields a styrene product of at least 99% or even at least 99.5% purity, and preferably the column will give this product and a recycle stream of less than about 3%, preferably less than 1% styrene based on C_8 aromatics when distilling the product resulting from the dehydrogenation at about 33% ethylbenzene conversion. Such a column was used in the examples which follow. Operation according to the process of this invention results in an increased ethylbenzene feed purification column capacity of 21% when 97% rather than 99.5% ethylbenzene is used, and at the same dehydrogenation conversion level gives 21% more styrene.

The process can be more readily understood by reference to the figure showing a flow sheet of the process.

Crude ethylbenzene feed enters the primary tower 1 and is purified by removing xylenes as the bottom product and taking off ethylbenzene, xylene and lighter materials over-

head. This overhead is joined with the recycle stream from the dehydrogenation system and the combined material is passed into distillation column 2. In column 2, benzene and toluene are removed overhead and ethylbenzene and xylenes are taken as a bottom product. As an alternative mode of operation, the ethylbenzene and xylene from column 1 may by-pass the benzene-toluene separation column 2 and go directly to dehydrogenation reactor 3, especially if the overhead from column 1 is essentially devoid of benzene and toluene. The bottom product from column 2 enters the dehydrogenation reactor 3 wherein ethylbenzene is converted to styrene. The dehydrogenation reactor effluent is separated in recycle distillation column 4. The high purity styrene product is recovered as the bottom product from column 4 and the overhead stream containing styrene, xylene, ethylbenzene, benzene and toluene is recycled to column 2.

Purification of the styrene may take place in the continuous finishing distillation tower 5 which has a highly pure styrene overhead product and a styrene and poly-

styrene bottoms product and batch finishing column 6, which has a styrene overhead product and a polymer bottoms product.

The following examples illustrate the process of this invention.

Example 1

An ethylbenzene feed was converted to styrene in equipment of the type described. Crude ethylbenzene feed was first separated from xylene to give a feed containing 2% xylene, based on C_8 aromatics. Benzene and toluene impurities were removed in a second distillation. The bottoms products from the benzene-toluene column were then sent to a dehydrogenation reactor containing a dehydrogenation catalyst containing approximately 90% Fe_2O_3 , 4% Cr_2O_3 , and 6% K_2CO_3 , and from there to a recycle column which removed xylene, ethylbenzene, benzene and toluene impurities from the styrene and recycled them to the benzene-toluene column. Flow rates, stream compositions, and reactor compositions for this run are shown in Table I.

TABLE I

Composition	Flow Rates (Parts by Weight/Hr.)					
	Ethylbenzene Feed To B-T Twr. 2	Recycle and Liquid From Vent Condenser To B-T Twr. 2	Benzene-Toluene Tower 2			Vent Gas From Dehydrogenation
			Feed	OVHD To Refinery	Bottoms To Reactor	
H ₂						5.67
C ₁						1.03
C ₂						0.82
C ₃						0.11
C ₄						10.27
Paraffin.....	0.52	1.68	2.20	0.15	2.05	
Benzene.....		6.52	6.52	6.52		
Toluene.....	13.88	15.61	28.99	28.99		
Ethylbenzene.....	163.30	146.07	309.37	4.24	305.13	
M-P Xylene.....	3.80	34.15	37.95	0.29	37.66	
Styrene.....		15.58	15.58		15.58	
Polymer.....						
Total.....	181.00	219.50	400.59	34.59	366.00	17.90

Composition	Flow Rates (Parts by Weight/Hr.)					
	Recycle Tower 4				Finishing Tower 5	
	Feed	OVHD Vapor To B-T Twr. 2 Via Vent Cond.	OVHD Liquid To B-T Twr. 2	Bottoms To Finishing Tower 5	OVHD Product	Bottoms To Batch Still 6
H ₂						
C ₁						
C ₂	0.14					
C ₃						
C ₄						
Paraffin.....	1.68	0.41	1.08			
Benzene.....	6.52	3.80	1.95			
Toluene.....	15.61	6.74	9.87			
Ethylbenzene.....	146.17	30.00	116.39	0.10	0.10	
M-P Xylene.....	34.72	6.62	27.06	0.57	0.57	
Styrene.....	150.41	2.43	18.14	134.85	133.60	1.25
Polymer.....	1.25			1.25		1.25
Total.....	368.56	50.00	169.59	136.77	134.27	2.50

Reactor Conditions		Reactor Feed Composition		Weight Percent
Fresh Feed (parts/hr.).....	168	Paraffins.....	0.56	
Recycle (parts/hr.).....	196	Toluenes.....	1.53	
Total Reactor Feed (parts/hr.).....	366	Ethylbenzene.....	83.37	
Total Steam to Reactor (parts/hr.).....	830	M-P Xylenes.....	10.29	
Steam Temp., °F.....	1,400	Styrene.....	4.25	
Reactor Inlet, °F.....	1,140	Total.....	100.00	
Reactor Outlet, °F.....	1,090			
Conversion Per Pass, Mole percent.....	45			
Weight Hourly Space Velocity, #/H EO/# Cat.....	0.66			

18.40 parts of the vent gas are products of the water gas reaction.

Example II

The process of Example I was repeated using an ethylbenzene feed containing 4% xylene based on C_8 aromatics. Flow rates and conditions are shown in Table II.

TABLE II

Composition	Flow Rates (Parts by Weight/Hr.)				
	Ethylbenzene Feed To B-T Twr. 2	Recycle and Liquid From Vent Condenser To B-T Twr. 2	Benzene-Toluene Tower 2		
			Feed	OVHD To Refinery	Bottoms To Reactor
H ₂					5.81
C ₁					1.16
C ₂					0.81
C ₃					6.16
CO ₂					12.26
Paraffin	1.31	2.02	3.33	0.88	2.44
Benzene		7.76	7.76	7.76	
Toluene	10.00	21.63	31.63	24.51	7.02
Ethylbenzene	171.70	133.35	305.05	50	304.55
M-P Xylene	6.99	57.80	64.79	0.03	62.83
Styrene		23.16	23.16		23.16
Polymer					
Total	190.00	250.00	440.00	33.68	405.9

Composition	Flow Rates (Parts by Weight/Hr.)				
	Recycle Tower 4			Finishing Tower 5	
	Feed	OVHD Vapor To B-T Twr. 2 Via Vent Cond.	OVHD Liquid To B-T Twr. 2	Bottoms To Finish- ing Tower 5	Bottoms To Batch Still 6
H ₂					
C ₁					
O ₂	0.20				
C ₃					
CO ₂					
Paraffin	2.02	0.53	1.64		
Benzene	7.76	3.98	2.48		
Toluene	21.63	7.59	12.26		
Ethylbenzene	133.35	25.25	113.86	0.10	0.10
M-P Xylene	57.80	9.69	45.58	0.63	0.63
Styrene	171.45	3.74	24.68	143.29	141.53
Polymer	1.94		1.94		
Total	396.15	50.00	200.00	145.98	142.26

Reactor Conditions		Reactor Feed Composition	
Fresh Feed (parts/hr.)	184	Paraffins	0.50
Recycle (parts/hr.)	222	Toluene	1.95
Total Reactor Feed (parts/hr.)	406	Ethylbenzene	75.08
Total Steam to Reactor (parts/hr.)	909	M-P Xylenes	15.48
Steam Temp., ° F.	1,388	Styrene	6.94
Reactor Inlet, ° F.	1,165	Total	100.00
Reactor Outlet, ° F.	1,112		
Conversion Per Pass, Mole percent	47.9		
Weight Hourly Space Velocity, #/H H ₂ O/# Cat.	0.62		

¹ 10.16 parts/hr. of the vent gas are products of the water gas reaction.

It is claimed:

1. In the process of producing styrene of at least 99% purity based on C_8 aromatic hydrocarbons from a C_8 aromatic hydrocarbon feed stream consisting essentially of xylene and 95 to 98.5% ethylbenzene based on the C_8 aromatics which consists essentially of combining said C_8 aromatic hydrocarbon with a C_8 aromatic recycle stream, dehydrogenating said combined C_8 material at a temperature of about 1000 to 1200° F. to produce styrene by dehydrogenation of ethylbenzene, removing the high purity styrene product from the reaction effluent and recycling remaining C_8 aromatic effluent to the dehydrogenation

reaction as said recycle stream, the conversion of ethylbenzene in said reaction being about 25 to 70% and sufficient to crack xylenes to lower boiling materials in an amount essentially equal to the amount of xylene in the C_8 aromatic hydrocarbon feed stream minus the xylene in the high purity styrene product.

2. The method of claim 1 wherein the ethylbenzene conversion is about 30 to 60% and the styrene product is at least 99.5% pure based on C_8 aromatic hydrocarbons.

3. The method of claim 2 wherein the recycle stream is separated from the styrene product in a distillation column which gives a recycle stream of less than 3% styrene when distilling the product stream resulting from the dehydrogenation at about 33% ethylbenzene conversion.

4. The process of claim 3 wherein the dehydrogenation is at a temperature of about 1050 to 1175° C.

5. The method of claim 2 wherein the dehydrogenation is conducted in the presence of a catalytic amount of a catalyst consisting essentially of Fe_2O_3 , Cr_2O_3 and K_2CO_3 .

6. The process of claim 5 wherein the C_8 aromatic hydrocarbon feed contains 96 to 97.5% ethylbenzene based on C_8 aromatics.

7. The method of claim 1 wherein said xylene comprises a mixture of meta and para xylenes.

References Cited by the Examiner

UNITED STATES PATENTS

2,376,709	5/1945	Mattox	260—669
2,963,518	12/1960	Amos et al.	260—672
3,093,694	6/1963	Soderquist et al.	260—669

DELBERT E. GANTZ, *Primary Examiner*.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,308,179

March 7, 1967

John A. Scott

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 75, for "1175° C." read -- 1175° F. --.

Signed and sealed this 7th day of November 1967.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents

Nov. 8, 1960

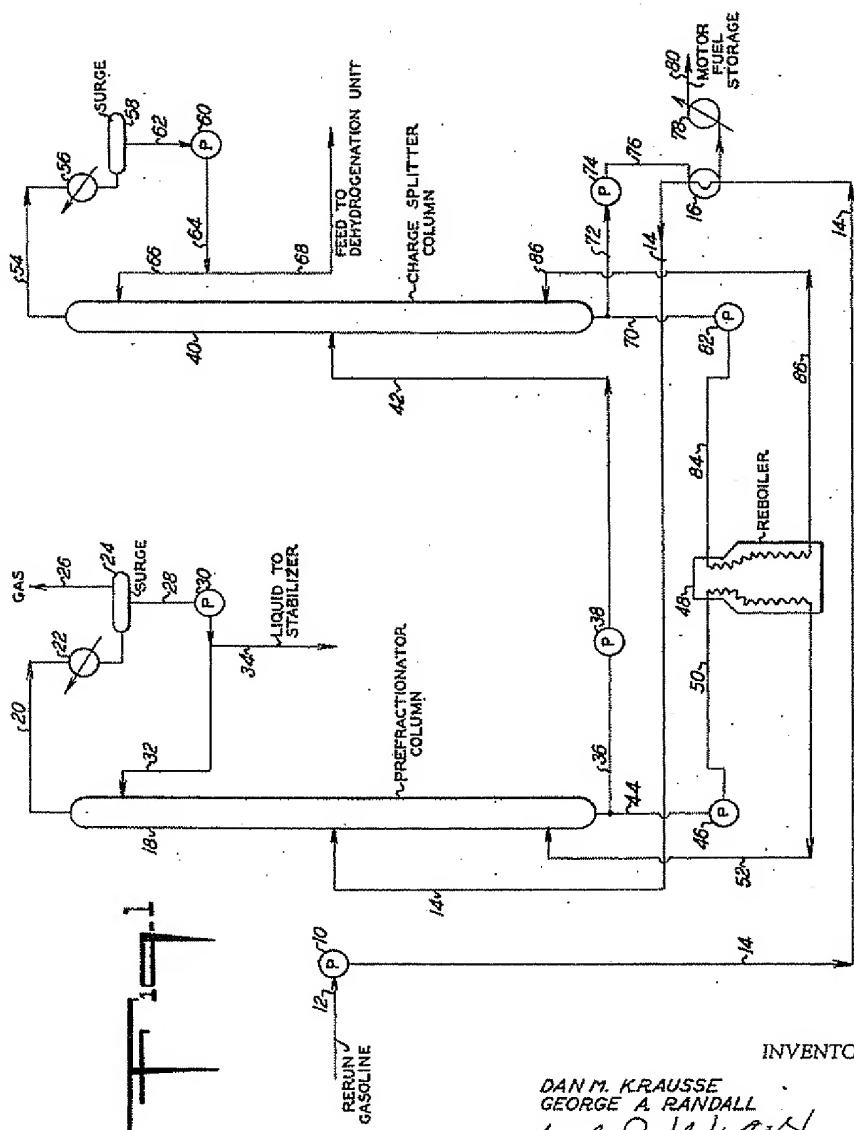
D. M. KRAUSSE ET AL

2,959,626

PROCESS FOR THE PRODUCTION OF STYRENE-GRADE ETHYL BENZENE

Filed July 15, 1957

5 Sheets-Sheet 1



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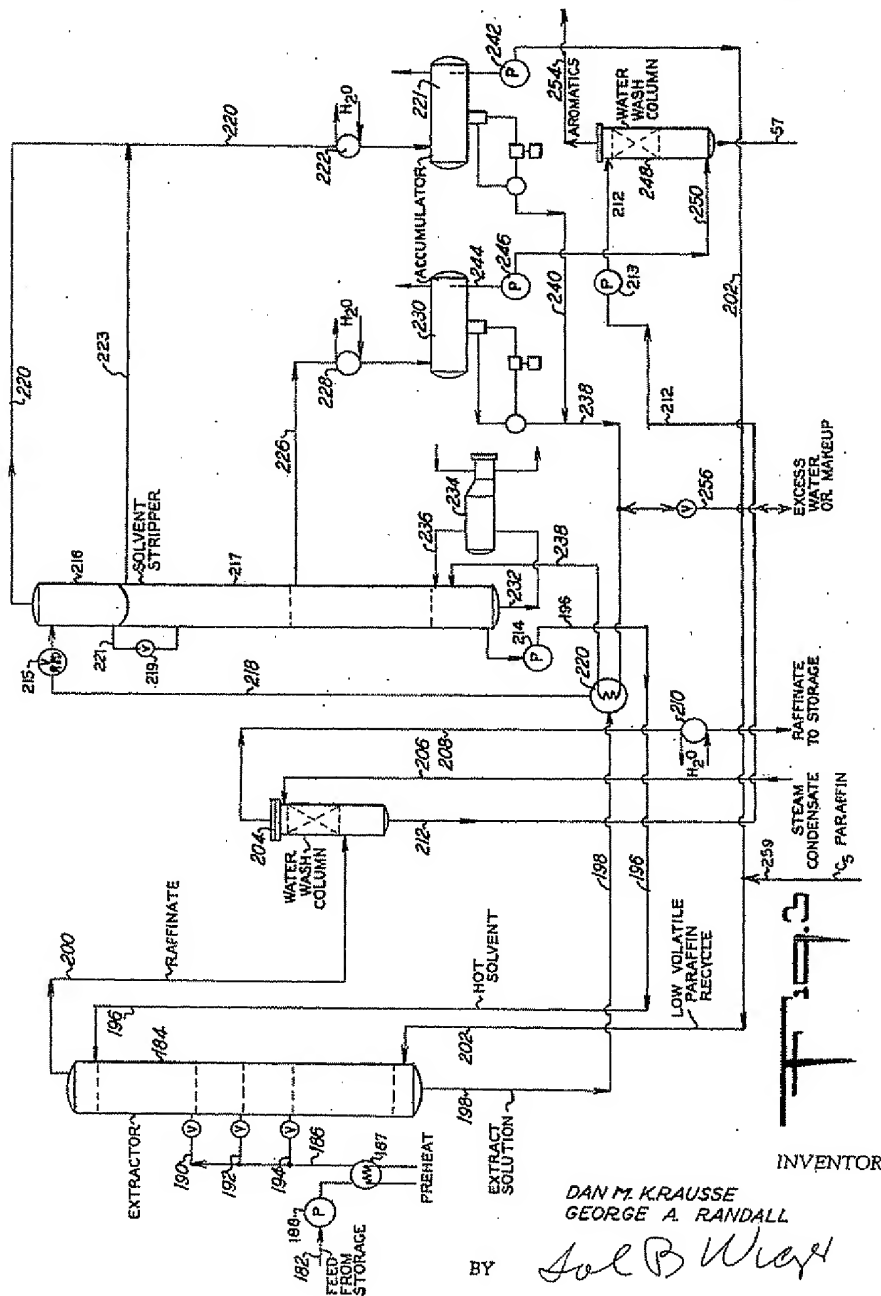
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2,959,626

PROCESS FOR THE PRODUCTION OF STYRENE-GRADE ETHYL BENZENE

Filed July 15, 1957

5 Sheets-Sheet 3



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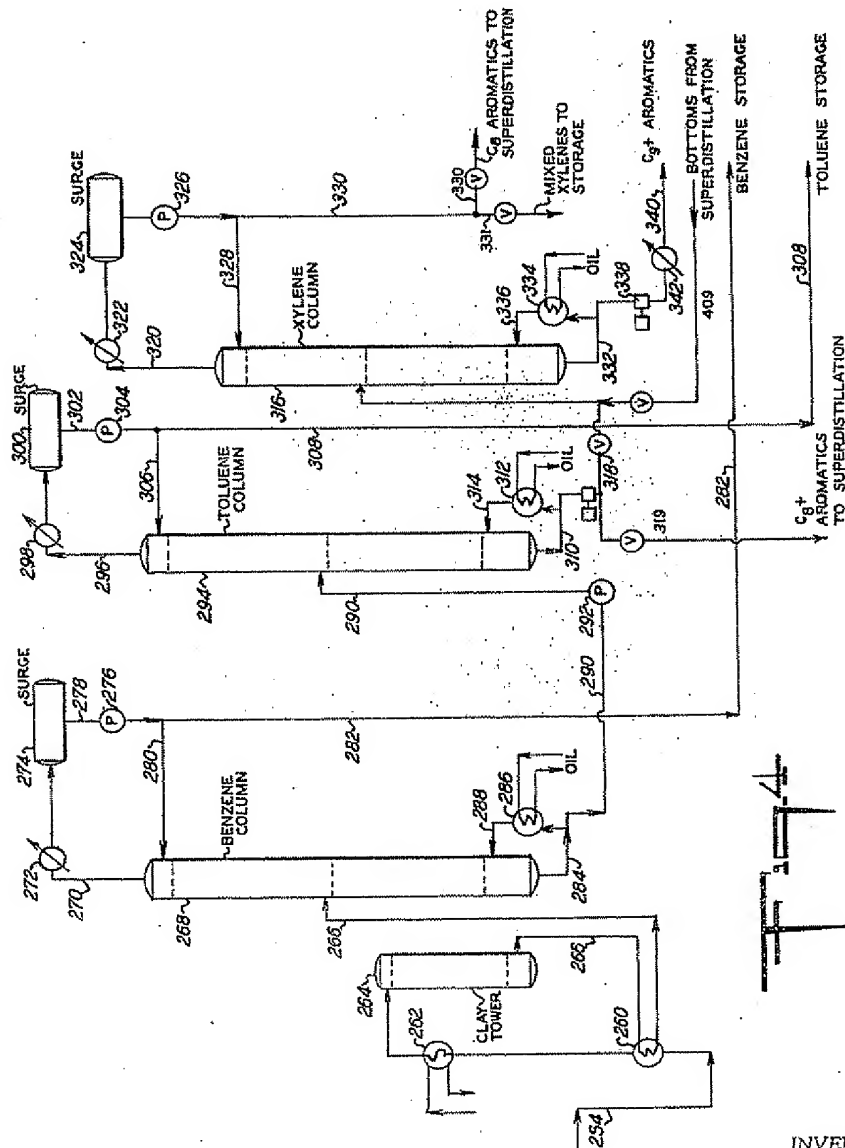
D. M. KRAUSSE ET AL

2,959,626

PROCESS FOR THE PRODUCTION OF STYRENE-GRADE ETHYL BENZENE

Filed July 15, 1957

5 Sheets-Sheet 4



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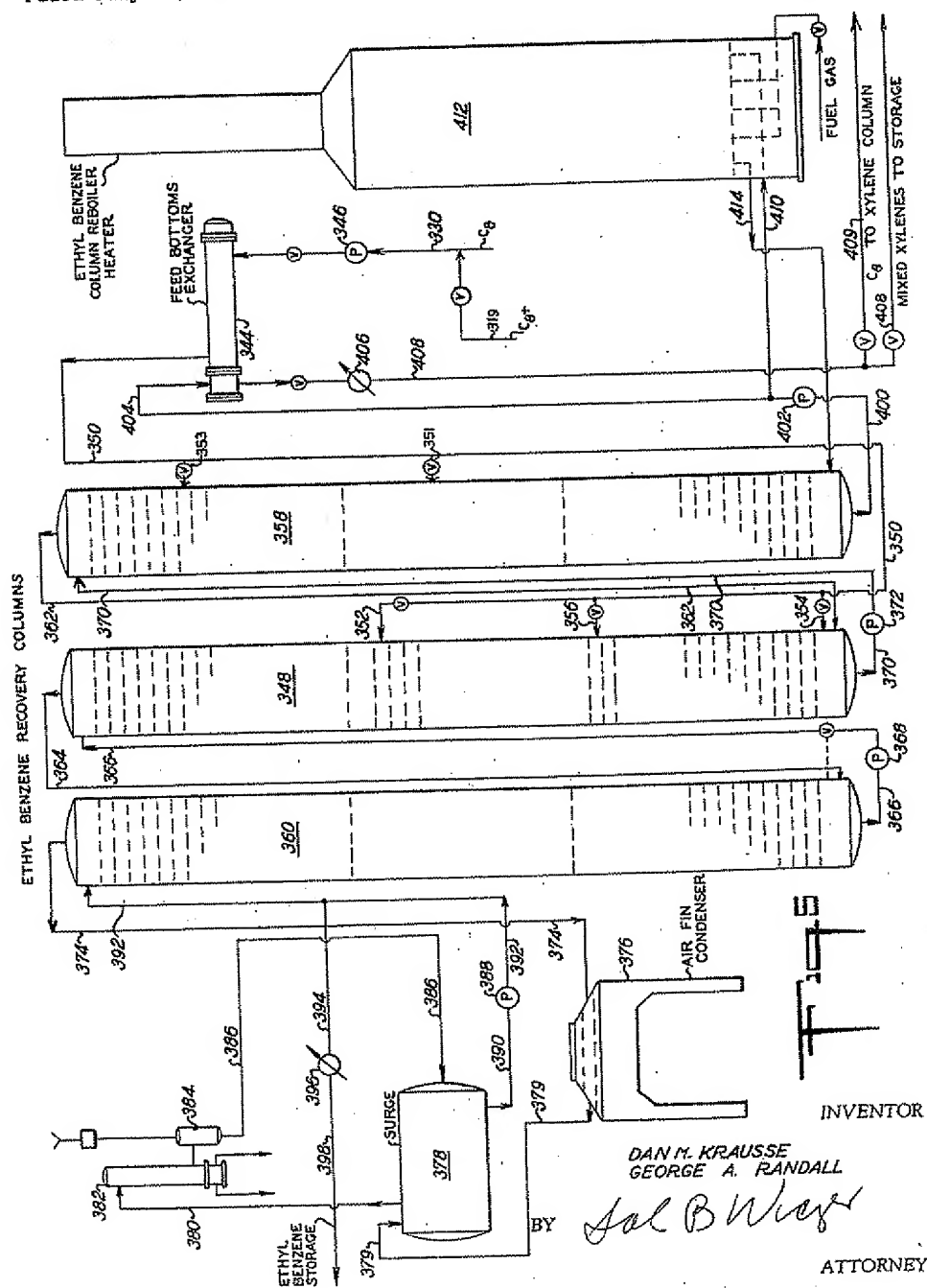
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2,959,626

5 Sheets-Sheet 5



1

2,959,626

PROCESS FOR THE PRODUCTION OF STYRENE- GRADE ETHYL BENZENE

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Filed July 15, 1957, Ser. No. 672,053

15 Claims. (Cl. 260-674)

This invention relates to a method for producing ethylbenzene in a degree of purity suitable for dehydrogenation to styrene. As a useful dehydrogenation stock for styrene production, the ethylbenzene hereof contains less than 1 volume percent of stable hydrocarbon impurity boiling in the C_8 aromatic hydrocarbon range, a range of about 130 to 140° C.

More particularly, the present invention provides a method and apparatus by which ethylbenzene may be superdistilled from a C_8 aromatics mixture in at least that degree of purity.

The invention also provides a method of producing a C_8 aromatics fraction mixture, containing less than 0.3% of non-aromatic hydrocarbon and comprising a useful charging stock for superdistillation to recover said ethylbenzene from a naphtha containing recoverable quantities of C_8 aromatics.

The invention further provides superdistillation apparatus comprising a plurality of two or more columns to effect the distillation of a C_8 aromatics fraction from which substantially pure ethylbenzene may be recovered using at least 150 plates or stages, and preferably from 200 to 400 plates or stages; and a critical distillation method of operating such apparatus including a reflux ratio exceeding 40:1 and preferably 60 to 150:1, whereby the ethylbenzene separated has a purity exceeding 99% for styrene production, and practically may exceed 99.995%.

In the production of styrene from ethylbenzene containing more than 1% of impurity by catalytic dehydrogenation, such impurity, if it is not decomposed during the reaction to components of remote boiling point and if it boils in the neighborhood of styrene or ethylbenzene, tends to prevent separation of styrene of adequate purity from the reaction products. A styrene produced from ethylbenzene containing more than about 1% of a stable hydrocarbon boiling in the C_8 aromatics range, such as 130-140° C., is useless for usual commercial purposes. If the ethylbenzene contains less than about 1% but more than 0.4% of such impurities, the styrene produced therefrom is useful for preparing synthetic rubber such as GR-S, but not commercially acceptable polystyrene polymer. For the latter purpose the ethylbenzene must contain less than 0.4% impurity. Thus, for commercial purposes, only styrene containing less than 0.4% is useful for direct polymerization to colorless plastic polystyrene, and that grade of styrene produced from such high purity ethylbenzene is known as polymer grade styrene. Styrene produced from ethylbenzene containing

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less than about 1% but more than 0.4% of stable hydrocarbon impurity, is known as rubber grade styrene.

The ethylbenzene produced by the present method has less than 1% of stable hydrocarbon impurity boiling in the C_8 aromatics range, such as from 130 to 140° C., and may be produced by the present method with impurities less than detectable, that is, ethylbenzene containing less than .005% impurity.

As a first step of this method, a C_8 aromatics mixture is obtained which contains less than 0.3% of non-aromatic hydrocarbon boiling in the C_8 aromatics range.

As a second step, this substantially pure C_8 aromatics mixture is superdistilled in a column comprising at least 150 distillation plates or stages, preferably 200 to 400 plates or stages at a reflux ratio exceeding about 40:1, preferably in the range of 60 to 150:1. The term reflux ratio as used herein is the ratio of reflux volume to net overhead product volume.

As a further feature of this invention, stable non-aromatic hydrocarbon components usually occurring with a C_8 aromatics extract fraction are displaced during the extraction of naphthas containing an extractable quantity of ethylbenzene by substituting lower boiling, usually non-aromatic hydrocarbon, for the higher boiling non-aromatic hydrocarbon components contained in the aromatic extract, thereby allowing production of a C_8 aromatics fraction of substantially pure aromatic components, and in any case, a C_8 aromatics fraction which critically contains less than 0.3% of stable non-aromatic hydrocarbon.

According to a preferred practice of this invention, a highly naphthenic naphtha feed stock is aromatized by catalytic dehydrogenation to produce a 40-60% aromatics yield, of which the C_8 fraction contains a recoverable quantity, usually more than 10% of ethylbenzene, and we averaged, according to our preferred procedure, about 27 to 34% of ethylbenzene in our C_8 aromatics fraction.

Ethylbenzene, prior to the present invention, was produced commercially by alkylation of benzene with ethylene. This catalytic alkylation is an expensive extra step in petroleum conversion to first form the pure benzene and ethylene and then convert them to ethylbenzene. The method of this invention distinguishes that common practice in completely avoiding this catalytic synthetic method by procedures, which in most economical aspect, are applied directly to raw petroleum naphthas first to form large quantities of ethylbenzene therein and then to isolate it from other hydrocarbon components.

It is known in the art that usual conversion of petroleum naphthas, particularly such as contain aromatics will, along with the benzene, toluene and xylene, contain some ethylbenzene. In many naphthas produced by petroleum conversion the aromatic content will vary widely and the ethylbenzene content thereof may vary slightly with the character of the raw naphtha feed stock, but the C_8 aromatic fractions separated therefrom average only about 11% of ethylbenzene.

The boiling point of ethylbenzene is so close to that of the xylene isomers contained in the C_8 fraction that separation of the mixture even by very fine distillation to obtain an ethylbenzene concentrate in sufficient purity to obtain an ethylbenzene of dehydrogenation quality to produce styrene, has not heretofore been possible. For

instance, in this ethylbenzene dehydrogenation, the unconverted ethylbenzene must be separated from the styrene produced, usually in less than 50% yield per pass, by distillation, and recycled for further dehydrogenation. Any stable hydrocarbon boiling in the C_8 aromatics range that is present is substantially unaffected and is not removed in the distillation to separate the residual ethylbenzene from the styrene produced, but a portion remains with the ethylbenzene fraction and thereby tends to build up in concentration therein and a portion remains with the styrene tending to increase the ethylbenzene content to further reduce the styrene purity, thereby reducing the quality of the styrene to below commercial acceptability as described above. Accordingly, the prior attempts to separate ethylbenzene from a C_8 aromatics fraction by a distillation of any character, resulted in such high impurity contents as to render the ethylbenzene useless for styrene production.

The separation of ethylbenzene in adequate degree of purity from a C_8 aromatics fraction is made possible by the present superdistillation only because substantially all stable non-aromatic hydrocarbon boiling in the C_8 aromatics range of about 130 to 140° C., and initially in quantity above about 0.3%, have been removed before that superdistillation is applied. The method of removing such stable hydrocarbon impurities, usually non-aromatics, according to the present invention, comprises extracting the aromatics with a polar type solvent from the mixed hydrocarbon feed stock containing a recoverable quantity of ethylbenzene, usually along with other aromatics. Such polar type solvent is characterized by having a relative selectivity in its solvent effect upon the feed stock hydrocarbon tending to dissolve more aromatics than non-aromatics. In usual operation the solvent to feed ratio may vary from 30 to 5:1.

During the extraction a continuous recycle of lower boiling hydrocarbon, boiling below the C_8 aromatics extract range, is maintained to pass such recycle through the aromatics rich solvent solution, thereby tending to displace from the extract any high boiling non-aromatic hydrocarbon dissolved in the aromatic extract solution, and substitute therefor the lower molecular weight non-aromatic hydrocarbon of the recycle. The extract solution is then distilled first to flash off dissolved low volatile non-aromatics for recycle to the aromatic rich solvent solution in the extractor. The aromatic hydrocarbon is then stripped from the solvent in a semi-steam distillation, separating a front end fraction containing any remaining quantity of volatile non-aromatics and some aromatics as overhead, also for recycle. Simultaneously a side stream of substantially 100% aromatics is removed from an intermediate portion of the stripping column.

In a subsequent distillation of the pure aromatics there is first separated benzene, then toluene and finally a C_8 fraction containing less than 0.3% and usually sub-

stantially no non-aromatic hydrocarbon. That C_8 fraction is then superdistilled to recover the substantially pure ethylbenzene as further described below.

It is occasionally found in certain virgin petroleum naphtha stocks that the C_8 aromatics fraction contains over 15% of ethylbenzene, and sometimes even as high as 25%. Accordingly, such stocks are useful as feed stock to the extractor when they are available, and while the whole range of the distillate may be used, it will be preferable, before extracting such virgin gasoline, to first separate therefrom a fraction which comprises a concentrate of the C_6 - C_8 aromatics.

It is also known that many gasoline conversion products contain ethylbenzene among their C_8 aromatics and such conversion products selected at random from many commercial petroleum conversion processes will average about 11% of ethylbenzene among their C_8 aromatics. Such catalytic conversion products, preferably after fractionating to isolate a concentrate of the C_6 - C_8 aromatics, may also comprise a useful feed stock to the extractor of the present invention.

It is found that if a naphtha comprising at least 25% naphthenes boiling in the range of 226-273° F. is catalytically dehydrogenated, large quantities of recoverable ethylbenzene, usually exceeding 15%, are found in the C_8 fraction of the aromatics formed therein and therefore, it is preferred to use as feed stock to the present extractor such catalytically dehydrogenated product.

A full boiling range petroleum naphtha boiling from 100 to about 400° F., typically about 140-175° F. IBP up to about 400° F. EP, may comprise the feed stock to the catalytic dehydrogenator, providing it initially contains at least 25% of naphthenes. The yields of C_8 aromatics in the aromatized product are also favorably affected by adjusting the feed stock to a high content of hydrocarbons containing at least 25% naphthenes boiling in the range of 226-273° F. Hence, the usual practice of this invention is to feed a naphtha to the catalytic dehydrogenator adjusted to have more than 25% of the feed stock composed of hydrocarbon comprising 25% naphthene boiling in this relatively narrow boiling range. It is found according to this preferred practice of this invention that very high, 27-34% yields of ethylbenzene are obtained when the feed stock to the catalytic dehydrogenator is supplemented by adding much more hydrocarbon boiling in the range of 226-273° F. and which comprises 35 to 55% naphthenes.

For purposes of comparing the yields of ethylbenzene available by the present preferred dehydrogenation procedure to increase the yields, to usual practices, two tables compiled by the Petroleum Refining Laboratory of Pennsylvania State University are reproduced. Table A shows ultimate analysis of the C_8 fraction of various straight run naphthas, and Table B shows a similar analysis upon various catalytically converted naphthas:

TABLE A

Relative amounts of C-8 aromatics present in naphthas

Relative amounts of C-8 aromatics present									
Source Naphtha	Straight Run Naphthas ¹								Average
	B.P., ° O.	Ponca City	East Texas	Bradford	Michigan	Winkler, Texas	Midway, Calif.	Conroe, Texas	
Volume percent of total C-8 Aromatics									
C-8 Aromatics:									
Ethylbenzene.....	136.2	18	17	9	15	25	24	8	17
P-xylene.....	138.4	9	13	16	12	39	16	16	17
M-xylene.....	139.1	48	48	55	51	26	38	57	46
O-xylene.....	144.4	25	22	19	22	10	22	19	20
Total.....		100	100	100	100	100	100	100	100

¹ Rossini, F. D., Haly, B. J., Streiff, A. J., Hydrocarbons from Petroleum, ACS Monograph 121, pages 440 and 462.

TABLE B
Catalytic naphthas

Type of Cracking	B.P., ° C.	Hydro-Forming	Fixed Bed		Fluid	
			2-Pass	3-Pass	Low Temp.	High Temp.
Reaction Temp., ° F.		925	850	875	800	975
Charging Stock		Selected Naphtha	Gas Oil + Heavy Distillate	Heavy Naph. from 2-Pass	Kerosene	Gas Oil
Volume Percent of Total C-8 Aromatics						
C-8 Aromatics:						
Ethylbenzene	139.2	11	13	9	13	13
P-xylene	138.4	18	19	20	18	20
M-xylene	139.1	47	46	52	45	49
O-xylene	144.4	24	20	19	24	18
Total		100	100	100	100	100

	38E 80 ¹	38H 65 ¹	38K 65 ¹	30Y 82 ¹	38R-Y 66 ¹	Avg. of
Reaction Temp., ° F.	975	975	975	1,000	975	10.
Charging Stock	Light Gas Oil	Light Gas Oil	Heavy Gas Oil	Gas Oil	Gas Oil	
Volume Percent of Total C-8 Aromatics						
C-8 Aromatics:						
Ethylbenzene	10	13	9	11	9	11
P-xylene	22	19	15	20	18	19
M-xylene	48	43	44	45	46	47
O-xylene	20	25	32	24	28	26
Total	100	100	100	100	100	100

¹ Vol. percent conversion.

It will be apparent from the data of Table A that there are some virgin naphthas which naturally contain usefully recoverable quantities of ethylbenzene and some contain relatively high quantities of ethylbenzene in the C-8 fraction whereby such is even more valuably recovered by the present method. With respect to data represented in Table B it is apparent that ethylbenzene available in the C₈ fraction of catalytic conversion stocks by any of the commonly practiced conversion methods is much lower than in Table A, the highest being only 13% of the C₈ fraction, and the average, only 11%, but these too may be usefully recovered. The yield of ethylbenzene by the preferred practice of the present invention may exceed the best of any available virgin or general catalytically produced gasoline stocks.

Accordingly, it is the preferred practice of this invention to aromatize a narrow B.P. range high naphthenic naphtha fraction by catalytic dehydrogenation. The aromatization or dehydrogenation comprises passing the naphtha over a dehydrogenation catalyst, typically a platinum containing catalyst, at a temperature in the range of about 825-975° F. and at a pressure in the range of about 200-500 p.s.i.g. in the presence of at least 4 to 12 mols, preferably 6 to 8 mols of hydrogen per mol of hydrocarbon fed to the unit. The catalytic dehydrogenator comprises several catalytic contact chambers in which dehydrogenation catalyst is distributed for optimum contact with the hydrocarbon vapors and hydrogen mixture, the apparatus providing means for reheating the vapors at intermediate points between contact chambers to maintain the reaction conditions, there being several, such as 3 to 6 catalytic contact chambers in a dehydrogenation assembly.

The dehydrogenation yield comprises about 75-90 wt. percent of the feed stock, the other products formed comprising some 4-6 wt. percent of hydrogen gas, and

the balance, gases and light liquids separated in a stabilizer. The reaction product after stabilizing and splitting to remove lower volatiles contains at least 30% of aromatic hydrocarbon and usually ranges from about 40 to 60% before solvent separation.

The catalytic dehydrogenation product is stabilized to remove the volatile material which boils substantially below the C₆ aromatics, the product being generally fractionated to an initial boiling point of about 140-155° F. Thereafter the stabilized product is extracted with a polar type solvent in which the solvent tends to dissolve greater quantities of aromatics than non-aromatics.

The character of the solvent may vary widely and includes such typical solvents as lower alkylene glycols such as ethylene, propylene or butylene glycols, lower alkylene glycolethers such as diethylene glycol and dipropylene glycol, furfural, phenol, liquid sulfur dioxide, liquid ammonia, nitrobenzene, aromatic amines such as aniline or toluidine, lower alkyl (1-6 carbon atom) primary, secondary and tertiary amines, and corresponding lower alkanol amines such as tri methyl amine, di ethyl amine, di butyl amine, di ethanol amine, tri ethanol amine and the like, and other polar solvents known in the petroleum extraction art, as well as mixtures thereof, may be used as the solvent. Generally the solvent is modified to impart a small water content for purposes of adjusting its selectivity, primarily to reduce its solvent power for non-aromatic hydrocarbon.

The solvent extraction is usually operated with continuous countercurrent flow of hydrocarbon to be extracted and solvent, with aromatic rich solvent being withdrawn from one end of the extractor and raffinate at the other. A continuous displacement from the extract of high boiling non-aromatic hydrocarbon by lower boiling non-aromatic hydrocarbon is effected by continuously introducing low boiling non-aromatic hydrocarbon into

the extract. The principle here followed to effect a desirable extraction of the aromatic hydrocarbon is based upon the fact that, whatever may be the absolute solubility of non-aromatics in the solvent solution of extracted aromatics, that solvent solution of aromatics has a greater solvent power for non-aromatic hydrocarbon of lower molecular weight than for similar non-aromatic hydrocarbon of higher molecular weight. By continuously passing more volatile lower molecular weight hydrocarbon into the solvent solution of aromatics, any higher molecular weight higher boiling non-aromatic hydrocarbon tends to be displaced from the extract solution into the raffinate and be replaced by the lower boiling non-aromatic hydrocarbon. Thus, the extract solution of aromatics in the polar solvent obtained from this extraction has its non-aromatic content of hydrocarbon composed substantially entirely of low boiling hydrocarbon. In operation of this extraction the low boiling hydrocarbon will be selected to boil below the C_8 aromatics range, and, to aid in practical economical recovery of other aromatics, even below the C_6 aromatics. The total hydrocarbon content is thereafter stripped from the solvent by distillation, both aromatic and non-aromatic hydrocarbon, and because of the substantial difference in boiling points the more volatile lower boiling non-aromatic hydrocarbon may readily be separated from the aromatics. The low boiling hydrocarbon usually boils below 140°C .

In a preferred procedure, a lower alkylene glycol ether, such as diethylene glycol or dipropylene glycol, and usually mixtures with a small quantity of water are used as the selective polar type solvent. The solvent is contacted countercurrently with the feed in usual ratio of 30 to 5 parts, preferably 10 to 15 parts, of solvent to 1 part by volume of hydrocarbon feed to be extracted. Obviously any higher ratio could be used with corresponding loss of economy in the process. Such solvent is preferred because it allows the extraction operations to be carried out at substantially raised temperatures and pressures for optimum efficiency. It allows easier separation of the hydrocarbon from the solvent, the more volatile non-aromatics by flashing, and the aromatics in a subsequently applied semi-steam type of stripping with good heat economy. The pure aromatics are readily taken off of a stripping column as a side stream from an intermediate position of the stripping column with any front end content of more volatile non-aromatic hydrocarbon passing overhead.

It is preferred, for ready volatilization of the non-aromatics from the aromatic extract hydrocarbon, to use as non-aromatic displacement feed, a low volatile substantially saturated lower paraffin hydrocarbon, predominantly C_5 paraffins or a C_5 fraction which may contain minor quantities up to about 20% of C_4 and C_6 paraffins, and as a typical C_5 fraction, the feed for displacement to the extractor will usually contain some of both. Such low boiling non-aromatics after separation from the aromatics is recycled to the extractor for continuously displacing heavier non-aromatics from the extract into the raffinate. The total non-aromatic recycle may vary widely from about 1 to 20 volume percent per volume of the extract solution, usually 1 to 5%. Since that volatile non-aromatic hydrocarbon distillate which dissolves in the aromatic solvent solution may be recovered simultaneously with the stripping of the aromatics from the solvent in a stripping column, with the aromatics taken off as a side stream, the stripping in the column may be adjusted to take along with the non-aromatic overhead some 5-10% aromatics. Thereby the side stream aromatic taken off from the column may comprise substantially 100% pure aromatics, and the small 5-10% quantity of aromatics taken overhead with the more volatile non-aromatics become recycled and continuously recovered with the extract in the extractor.

In recycling of the low volatile substantially non-aromatic

fraction, it is preferred to pass the same upwardly into the bottom of a continuously descending extract solution formed in a vertical column, from which the raffinate is removed at the top, whereby the non-aromatics introduced into the aromatics rich solution act as a continuous wash of the aromatic rich extract and displaces the high boiling non-aromatics upwardly into the column.

While the present invention is directed primarily to production of substantially pure ethylbenzene, inasmuch as the aromatic fraction produced is substantially pure aromatics, it is desirable, for over-all economy of the process, to separate C_6 and C_7 aromatics in separate preliminary distillations, and then separate a pure C_8 fraction from the residual C_9 and higher aromatics. For this purpose the purely aromatic extract, after clay treatment to remove trace quantities of color forming impurities, is fractionated to separate benzene first, then toluene, and then fractionated to separate the C_8 fraction from the C_9+ bottoms. Hence, this preliminary fractionation is carried out under narrow boiling point range conditions, thereby to obtain a higher degree of purity for each of these C_6 and C_7 components. For instance, a benzene distillation column is used having at least 12 stages or plates, preferably about 35 to 45 stages and operated with a minimum reflux ratio of at least 1.3:1, preferably about 5 to 7:1, to remove the benzene. In such distillation benzene of 0.884 sp. gr. at 60°F . with a distillation range of 0.5 to 1°C . and a freezing point in the range of 5.3 to 5.45°C ., is produced.

In a similar manner toluene may be distilled from the residue of the benzene distillation by distilling in a column having more than 14 stages or plates, preferably from about 35 to 45 stages or plates, operated with a reflux ratio of at least 1.0:1, preferably from about 2.0 to 4.0:1. The toluene thereby produced as overhead may have a boiling point range of 0.5 to 1°C . and a sp. gr. at 60°F . of 0.872. It will be apparent with these fine distillations that both benzene and toluene may be recovered in a reagent grade of purity greatly enhancing the economy of this process.

Either the total C_8 plus residue of the toluene distillation, or a C_8 fraction immediately distilled therefrom, is superdistilled in a column of at least 150 stages or plates, preferably 200-400 stages with a reflux ratio of at least 40:1, preferably 60-150:1 thereby to produce ethylbenzene as an overhead having at least the 99% purity as stated above. If the total C_8 plus residue is superdistilled, the bottoms residue of that superdistillation will consist of residual C_8 (mixed xylenes substantially free of ethylbenzene) and C_9+ aromatics. In this procedure the residue of such superdistillation consisting of xylene isomer and C_9+ aromatics may be returned to a xylene distillation column from which the isomeric mixture of pure xylenes may be separated from the C_9+ hydrocarbon.

As an alternate procedure the bottoms or residuum of the toluene distillation may be first distilled in a wide boiling range of $4-10^\circ\text{C}$. merely to separate in an ordinary distillation the C_8 aromatics from the C_9+ and, thereafter, this wide, $4-10^\circ\text{C}$. boiling range C_8 overhead fraction may be superdistilled.

Within the limits of minimum distillation stages and reflux ratio stated for the superdistillation, ethylbenzene may be separated from the C_8 aromatics mixture, if the stable non-aromatic hydrocarbon content in the C_8 boiling range is less than 0.3%, in purity of at least 99%. In preferred ranges of conditions given, that is, with more than 200 stages and a reflux ratio of more than 60 to 1, the ethylbenzene obtained has a purity of 99.995%.

The invention is further described with reference to

a specific embodiment illustrated in the drawings, wherein:

Fig. 1 illustrates diagrammatically a feed preparation section,

Fig. 2 illustrates a catalytic dehydrogenation-aromatizer unit,

Fig. 3 illustrates an extraction section,

Fig. 4 illustrates a benzene, toluene and mixed xylene distillation unit, and

Fig. 5 illustrates a super-distillation unit to separate ethylbenzene.

A raw feed stock to be catalytically dehydrogenated to form aromatics therein may be first separated into a naphtha boiling in the range of 100 to 400° F., preferably a narrower boiling point range high naphthene naphtha of approximately C₆-C₉ hydrocarbon. The formation of such feed stock is illustrated in the feed preparation section Fig. 1. For this purpose, a wider boiling range naphtha, which may be a virgin gasoline or a re-run gasoline, preferably highly naphthenic or of gasolines blended to include a substantial quantity of naphthenic hydrocarbon, is drawn by pump 10 from inlet line 12, and passed by way of line 14 and a heat exchanger 16, to a prefractionator column 18, in which the more volatile ends boiling below 100° F., and usually below the desired initial boiling point feed stock, preferably below the range of 140-175° F., are removed. These light volatile vapors pass overhead of the column 18 through line 20, are cooled to condense a substantial portion to liquid in heat exchanger 22, and then are sent to surge drum 24 from which uncondensed gases are removed through line 26. The condensed liquid is withdrawn through line 28 by pump 30, and part of the liquid is returned by way of line 32 to the top of the prefractionator column 18 as reflux, and the remaining portion is sent to storage via a stabilizer (not shown) through line 34.

A portion of the prefractionator bottoms are withdrawn through line 36, by pump 38 and sent to the center of a charge splitter fractionating column 40, by way of line 42. Another portion of the prefractionator bottoms are withdrawn through line 44 by pump 46 and passed through a reboiler 48 by way of line 50, and returned as a hot vapor mixture to the bottom of the prefractionator column, by way of line 52.

The charge splitter column 40 is operated to pass overhead vapors by way of line 54 at a temperature boiling in the useful feed stock fraction range, that is, below the end point of about 400° F. The desired overhead vapors are condensed to liquid by heat exchanger 56, passing to surge drum 58, from which it is withdrawn by pump 60 by way of line 62, and passed through line 64. The distillate in line 64 is divided, a portion being returned by way of line 66 to the top of the charge splitter column 40 as reflux, and the remainder sent through line 68 as the desired raw feed stock to be fed to the catalytic dehydrogenation unit illustrated in Fig. 2.

The charge splitter bottoms are withdrawn from the bottom of the column 40, a portion being drawn through line 72, by pump 74, and sent through heat exchanger 16, by way of line 76, and then through a cooler 78, finally passing out of the system, such as to storage, by way of line 80. Another portion of the bottoms drawn through line 70 by pump 82 is passed through reboiler 48, by way of line 84, and returned to the lower end of charge splitter column 40 by way of line 86 as a hot vapor mixture to effect the distillation in column 40.

The charge formed passing through line 68 has been adjusted to the boiling point range of 100 to 400° F., preferably a narrower range such as 150 to 310° F. It will contain at least 25% of naphthenes, preferably substantially higher, up to about 60%. It may contain a few percent of aromatics, usually not more than 15%,

and the remainder is substantially paraffins. The following table illustrates a useful range as well as a practical preferred range of feed stock characteristics:

TABLE C
Feed stock to catalytic dehydrogenator

	Useful Range	Preferred Range
Gravity, °API at 60° F.	68-80	68-80
Initial Boiling Pt., °F.	100-175	150-170
10% °F.	160-200	170-190
50% °F.	210-300	210-220
90% °F.	240-360	240-250
End Point, °F.	285-400	285-310
Vol. Percent Paraffins	25-75	45-55
Vol. Percent Naphthenes	25-60	35-55
Vol. Percent Aromatic	0-15	5-15

Of this feed stock, the hydrocarbon that typically forms the benzene in the catalytic dehydrogenation product boils in the range of 150-185° F.; the hydrocarbon which forms toluene boils in the range of 185 to 226° F.; hydrocarbon which forms ethylbenzene and isomeric xylenes boil in the range of 226-273° F.; and the hydrocarbon which forms C₉+ aromatics boils in the range of 273-400° F. For present purposes, to form ethylbenzene, it will be apparent that the feed stock has as its preferred components, naphthenic hydrocarbon boiling in the range of 226 to 273° F. Thus, the feed stock passing through line 68 in the feed preparation section, may have been adjusted to the boiling range of 226 to 273° F., or the wider range feed stock such as 100 to 400° F., as described in the operation of Fig. 1 may be used; or this wide boiling range stock may be further enriched with naphthenic hydrocarbon boiling in the range of 226 to 273° F. It is accordingly possible not only to produce the high ethylbenzene content C₈ aromatic fraction by catalytic dehydrogenation of a selected feed stock, but also control the quantity and type of other aromatics that may be produced simultaneously as by-product for enhancing over-all economy of the process by judicious enrichment of the feed stock with desired boiling range naphthenic hydrocarbon.

Referring to Fig. 2, the selected raw feed stock from line 68, under pressure of pump 88, passes through line 90 together with hydrogen from line 102 supplied in proportion of from 4-12 mols, preferably 6 to 8 mols, of hydrogen per mol of hydrocarbon, through heat exchanger 100 to heater 104 by way of line 106. The heater 104 heats the hydrocarbon to the range of about 850-975° F., preferably 910-930° F., to a pressure of 200-500 p.s.i.g., preferably 420-460 p.s.i.g., and the hot vapor charge is passed by way of line 108, to the first reactor 110, in which the vaporized charge is contacted with a dehydrogenation catalyst, usually platinum. The reaction is endothermic, the charge being cooled substantially as the product becomes dehydrogenated to form aromatics. The vapors are withdrawn from the bottom of the reactor 110 through line 112 and sent to reheater 114, returning after reheating to the desired reaction temperature to a second reactor 116, by way of line 118. The second stage reaction product withdrawn from the bottom of reactor 116 is again passed to reheater 114, by way of line 120, and returned after reheating to the top of the third reactor 122, by way of line 124. The third stage reaction mixture withdrawn from the bottom of reactor 122, is again heated in reheater 114, by way of line 126 and sent to the fourth stage reactor 128, by way of line 130.

The fourth stage reaction mixture withdrawn from the bottom of reactor 128, by way of line 132, is sent through heat exchanger reboiler 134 and then through heat exchanger 100, by way of line 136, is cooled in a second heat exchanger 138 to condense liquids and sent to a gas and liquid separator 140, by way of line 142. A portion

of the uncondensed vapors, mostly hydrogen, are withdrawn from the system through vapor line 144 and a remaining portion sent to a compressor 146 by way of line 148, to recompress the gases, mostly hydrogen, to reaction pressure of about 200 to 500 p.s.i.g., preferably 420 to 460 p.s.i.g., returning the same to the raw incoming feed stock, passing through line 90, by way of line 102.

The condensed liquid reaction product is withdrawn from separator 140, by way of line 150, passing through heat exchanger 152 and thence, by way of line 154, is passed to an intermediate point in a stabilizer column 156. In the stabilizer column, overhead vapors comprising volatile hydrocarbon boiling below the approximate range of 200 to 210° F., under a pressure of 150-200 p.s.i.g. are taken off through line 158, cooled substantially to condense a substantial portion to liquid in cooler 160, and then separated from uncondensed gases in the surge drum 162, the vapors being withdrawn through line 164 by way of pressure regulating valve 163. The liquid is withdrawn from surge drum 162 by pump 166, by way of line 168, and a portion is sent to the top of the stabilizer column as reflux by way of line 170, and a portion is withdrawn as light overhead distillate and sent to storage by way of line 172. The aromatized bottoms from the stabilizer column 156 are withdrawn by way of line 174, and a portion is sent by way of line 176 to re-boiler 134 and returned as a hot vaporous mixture to the bottom of the stabilizer column through line 178. The remaining portion of stabilizer bottoms from line 174 are passed through heat exchanger 152 and then, after cooling in exchanger 180, are sent to storage by way of line 182.

In the catalytic dehydrogenation aromatizer section 25-60%, usually 45-53%, of the raw feed stock after stabilizing comprises aromatic hydrocarbon. The following Table D illustrates a useful as well as a preferred range of operating conditions in the catalytic dehydrogenation section:

TABLE D
Operating conditions dehydrogenation section

Equipment	Temperature, ° F.		Pressure, p.s.i.g.	
	Useful Range	Preferred Range	Useful Range	Preferred Range
Inlet No. 1 Reactor.....	890-975	910-930	200-500	420-460
Outlet No. 1 Reactor.....	810-925	810-860	-----	-----
Inlet No. 2 Reactor.....	890-975	910-930	-----	-----
Outlet No. 2 Reactor.....	810-925	845-870	-----	-----
Inlet No. 3 Reactor.....	890-975	910-930	-----	-----
Outlet No. 3 Reactor.....	810-925	875-905	-----	-----
Inlet No. 4 Reactor.....	890-975	910-930	-----	-----
Outlet No. 4 Reactor.....	810-950	890-920	150-500	320-350
Separator.....	35-135	80-105	100-450	300-360
Stabilizer Column:				
Top.....	190-250	200-210	100-250	120-200
Bottom.....	350-450	400-420	100-250	120-200
<hr/>				
			Useful Range	Preferred Range
Hydrogen to Hydrocarbon—Ratio.....			4-12	6-8
Yield:				
Total Dehydrogenation Product, Weight Percent.....			75-90	80-90
Hydrogen Gas, Weight Percent.....			4-6	4-6
Stabilizer O'head Liquid, Wt. Percent.....			5-12	5-12
Stabilizer O'head Gas, Wt. Percent.....			0.2-1.0	0.2-1.0

The catalytic dehydrogenation products obtained under the conditions set forth in Table D have the following characteristics after stabilizing. B.P. range 140-340° F., vol. percent paraffin 35-65, vol. percent naphthene 3-10, vol. percent aromatic 25-60. The ethylbenzene obtained from the C₈ aromatics contained therein ranges from 27 to 34% of the C₈ fraction. As stated above, similar ethylbenzene containing naphthas from other sources may be

used as feed stock to the extractor. Since this catalytic dehydrogenation produces such high ethylbenzene content in the C₈ aromatics, it is a preferred feed stock to the extractor.

The preferred extraction unit, here described, is designed for operation at raised temperatures, typically in the range of 220-325° F., preferably in the range of 280-300° F., and pressure in the range of 80 to 135 p.s.i.g., preferably 125-130 p.s.i.g. Under these conditions the lower alkylene glycol ethers are the most useful solvents, and we use, typically, diethylene glycol or dipropylene glycol or mixtures thereof, with small quantities, up to about 12%, preferably 5 to 10%, of water. When other solvents are used the system may be operated at lower or higher temperatures variable with the physical, such as the boiling point characteristics of the particular solvent.

In operation of such system, as illustrated in Fig. 3, the feed from storage, for example, the stabilized catalytic dehydrogenated product obtained as illustrated in Fig. 2, or other useful ethylbenzene containing feed stock as described, enters the extraction system through line 182 and is passed by pump 188, first through heat exchanger 187 to preheat the feed to a desired extraction temperature, such as 280-300° F., and thence, by way of line 186 to some preselected intermediate level of the extractor 184, such as through pipes 190, 192 or 194, and at a pressure such as from about 125 to 130 p.s.i.g. at which the system is operating.

Hot solvent at a similar temperature and pressure enters the top of extractor 184 through line 196 in preferred ratio of about 10-15 parts of solvent to about 1 of hydrocarbon feed. Simultaneously a light hydrocarbon reflux, typically a paraffinic refinery cut, is supplied to the bottom of the extractor 184 through line 202, the C₈ hydrocarbon being generally obtained as recycle from the stripper as explained further below. That paraffinic recycle in line 202 is supplied at about 1½ to 4½% of the solvent rate. The solvent and mostly dissolved aromatic hydrocarbon, with some lesser quantity of non-aromatic components, descend through the column as the extraction proceeds, so that an aromatic rich solvent solution concentrates at the bottom of the extractor 184, and an aromatics poor raffinate hydrocarbon ascends to the top of the extractor 184. The aromatics rich solvent solution is continuously washed by the light paraffinic C₈ hydrocarbon recycle from line 202, which tends to displace from the extract solution as a continuous wash, the heavier non-aromatics dissolved therein, replacing the same with the lighter C₈ hydrocarbon. Thus, the extract solution withdrawn from the extractor 184 through line 198 from which higher boiling non-aromatic hydrocarbon has been replaced by the lighter C₈ non-aromatic hydrocarbon of the recycle is substantially aromatic. The raffinate, as produced in the extraction, and taken off overhead through line 200, contains some of the undissolved recycle C₈ hydrocarbon together with the heavier displaced non-aromatic hydrocarbon from the extract, as well as the unextracted hydrocarbon remaining after contact of the raw feed with the solvent. That raffinate may further contain a small quantity of unextracted aromatic hydrocarbon.

The raffinate in line 200 is passed to a point near the bottom of water wash column 204, and the raffinate hydrocarbon introduced therein rises countercurrently to a supply of wash water introduced near the top of the column 204 by way of line 206. The washed raffinate is withdrawn from a point near the top of column 204 through line 208 and sent to raffinate storage after cooling in a heat exchanger 210. The wash water, together with small quantities of solvent removed from the raffinate, after descending to the bottom of the water wash column 204, is withdrawn through line 212, and sent to the top of an aromatics extract wash column 248, as impelled by a pump 213.

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The hot aromatics rich extract solution in the solvent, withdrawn from the bottom of extractor 184 through line 198, is first cooled to the range of 215–250° F., preferably 225–240° F., in heat exchanger 220, and then sent by way of line 218 to a point near the top of a solvent stripper section 216 by way of pressure reducing valve 215. In the solvent stripper 216, by reduction of pressures to below about 50 p.s.i.g., preferably to about 10–20 p.s.i.g., the volatile non-aromatic hydrocarbon (dissolved C_6 paraffin) components flash overhead as vapors through line 220, and the unvolatilized solvent solution of aromatics collecting in the bottom of the flashing section 216, are transferred by way of a float controlled valve 219 through line 221 to a point near the top of a solvent stripper section 217.

In the solvent stripper section 217 all of the aromatics and any of the residual non-aromatics which were not removed in the flashing applied in flashing section 216, are stripped from the bottom of the solvent stripper, a portion of the steam being obtained through line 238 by distillation in heat exchanger 220, and another portion from reboiled solvent heated in the boiler 234, and returned to the bottom of the stripper through line 236. Thus, the stripping in effect, is a semi-steam type stripping, obtained by passage of steam into the bottom of the stripper. At the top of the stripper any of the more volatile residual generally non-aromatic C_6 hydrocarbon is first vaporized and then passed overhead through line 223. Some of the more volatile aromatics are also allowed to pass overhead together with a substantial quantity of steam through line 223, and that overhead product in line 223 is rejoined with the non-aromatic hydrocarbon passing through line 220 as originally flashed from the solvent solution, and both components are cooled in heat exchanger 222 to condense them to liquid and passed to accumulator 224.

Since the non-aromatic hydrocarbons are the most volatile they are efficiently removed from the top of the column through line 223 together with about 5–10% of the most volatile aromatics, and the substantially 100% pure aromatic streams may be taken off of the stripper column 217 as a side stream through line 226, together with some steam. This mixture is cooled in heat exchanger 228 to condense the aromatics to liquid and passed to accumulator 230 together with small quantities of steam condensed to water therewith.

A portion of the solvent accumulating in the bottom of the stripper is withdrawn through line 232, passed to reboiler 234 and returned as a vaporous mixture to the bottom of the column through line 236 to supply the heat for stripping, and concentrate the solvent to contain the desired quantity of water. The remainder of the solvent is continuously withdrawn from the bottom of the stripper through line 196 by pump 214 and returned to the top of the extractor.

The accumulator tank 230, in which the stripped aromatics are collected, has the aromatics withdrawn therefrom by a take-off pipe 244, which passes the accumulated aromatics by way of line 250, as impelled by pump 246, to a point near the bottom of a water wash column 248. The aromatic hydrocarbon rises countercurrently in column 248 to water supplied to a point near the top thereof from line 212. The washed aromatics are withdrawn from the top of the water wash column 248 through line 254 for further processing as illustrated in Fig. 4.

Some water accumulating in a sump below the bottom of accumulator 224 is withdrawn through line 240 and sent to line 238 and returned to stripper 217 after first being vaporized to steam in exchanger 220, thereby furnishing additional steam for the semi-steam stripping operation.

The volatile hydrocarbon flashed overhead in flash column 216 and overhead from the top of stripping column 217, by way of line 220 and 223 to comprise mostly

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C_6 hydrocarbon with about 5–10% of more volatile aromatics, is removed from accumulator 224 from pump 242, and passed as continuous recycle to the bottom of the extractor 184 by way of line 202. From time to time additional paraffinic C_6 hydrocarbon may be supplied to the system by way of line 259 to pass the same into line 202 as needed.

Any excess water or deficiency of water is withdrawn, or supplied to the system by way of line 256 connecting with line 238. Wash water accumulated in the bottom of wash column 248 is withdrawn from the system by way of line 257.

The useful range as well as preferred operating characteristics of the solvent extraction system, illustrated in Fig. 3, are summarized in Table E:

TABLE E

Operating conditions of glycol ether extraction system

	Useful Range	Preferred Range
Extractor Temperature, ° F.	220–325	280–300
Extractor Pressure, p.s.i.g.	80–135	125–130
Stripper Bottom Temperature, ° F.	250–325	280–300
Stripper Top Temperature, ° F.	215–250	225–240
Stripper Flash Pressure, p.s.i.g.	0–50	10–20
Stripper Bottom Pressure, p.s.i.g.	0–25	5–10
Clay Tower Inlet Temp., ° F.	400–450	425
Clay Tower Inlet Pressure, p.s.i.g.	100–225	150–200
Clay Tower Outlet Pressure, p.s.i.g.	90–200	130–170
Recycle composition:		
C_6 Paraffin	70–100	75–90
C_7 Paraffin	0–20	1–10
C_8 Paraffin	0–20	1–10
Aromatic	0–10	5–10
Solvent Composition:		
Wt. Percent Water	2–12	5–10
Wt. Percent Diethylene glycol	65–66	68–65
Wt. Percent Dipropylene glycol	0–28	0–25
Raffinate:		
Gravity, ° API at 60° F.	67–73	67–73
Volume Percent Paraffins	80–95	80–95
Volume Percent Naphthenes	2–12	0–5
Volume Percent Aromatics	0–10	0–3

Referring to Fig. 4, washed solvent free aromatic extract passing through line 254, with or without intermediate storage, is preheated to heat exchanger 260 and further heated by heater 262 and sent through a clay treating tower 264 to remove slight quantities of impurities such as traces of color forming bodies. The clay treated extract leaves the clay tower through line 266 and, after passing through heat exchanger 260, is sent to a benzene distillation column 268. The benzene vapors passing overhead through line 270 are cooled in condenser 272. The condensate accumulates in the surge drum 274 from which it is withdrawn by pump 276, by way of line 278, and a large portion is returned to the top of the column through line 280 as reflux, and a product portion is withdrawn to storage as benzene by way of line 282. For production of reagent grade benzene, a column of at least 12, preferably 35 to 45 stages or plates are used with a minimum reflux ratio of 1.35:1, preferably 5 to 7:1 is used, whereby benzene of a purity of 0.5–1° C. boiling range may be obtained. The benzene distillation column bottoms are withdrawn through line 284, a portion being passed to reboiler 286, and returned to the still after heating through line 288, and a portion sent through line 290, as impelled by a pump 292 and passed to a toluene distillation column 294.

The overhead vapors of the toluene column 294, passing through line 296 are condensed by condenser 298 and accumulated in surge drum 300. A portion of the condensate withdrawn through line 302 by pump 304 is returned to the top of column 294 through line 306 as reflux, and a portion of the toluene product is sent to storage through line 308. Again, by maintaining a minimum reflux ratio of 1.0:1, preferably 2.0–4.0:1, and using a column of at least 14, preferably 35 to 45 stages or plates, a nitration grade toluene having a distillation

range of 1° C. or less may be produced. The toluene column 294 bottoms, withdrawn through line 310 has a portion passed to reboiler 312 and returned to the column through line 314 and a portion is sent to a xylene distillation column 316, by way of line 318; or alternatively is sent by way of by-pass line 319 directly to superdistillation of Fig. 5 described below.

The C_9 vapors taken overhead through line 320 from the column 316 in a temperature range of 130 to 140° C. are condensed by condenser 322 and passed to surge drum 324, of which a portion is returned by pump 326 to the top of the column 316 by way of line 328 as reflux, and a portion is sent to the superfractionation column Fig. 5 via storage. The C_9 bottoms, withdrawn from the bottom of the xylene column 316 through line 332 has a portion passed through reboiler 334, from which a vaporous mixture is returned through line 336, and a portion is sent by pump 338 to C_9+ bottoms storage by way of line 340 after cooling in exchanger 342. The xylene column 316 has at least 10, preferably 25-35 stages or plates, operating at a reflux ratio of at least 0.15:1, preferably 0.3 to 0.5:1. In this C_9 product distillation, the overhead product has a distillation range of about 4-10° C.

The C_8 overhead, when operating on the narrow range feed stock to the catalytic dehydrogenator, as defined in "Table C" above will comprise about 0-10% toluene, about 27-34% ethylbenzene and the remainder, mixed xylene isomers, of which the metaxylene is present in predominant portion, about twice that of either of the other xylenes, the para and ortho being in about equal quantities. The mixed C_8 overhead, passed to the ethylbenzene recovery section shown in Fig. 5, is substantially 100% aromatic and usually contains less than 0.05% non-aromatics, well below the critical 0.3% limit. This raw feed stock enters the ethylbenzene recovery system in Fig. 5 through line 330 either directly as leaving the xylene column of Fig. 4 or after intermediate storage.

In an alternate procedure the ethylbenzene may be removed directly by superdistilling the C_8+ bottoms following toluene removal in column 294. Small quantities of toluene boiling much lower than the C_8 aromatics do not interfere with the separation and can be tolerated in reasonable quantities. As being substantially more volatile than either ethylbenzene or styrene, it is simply distilled from the ethylbenzene or a subsequent mixture with styrene. In fact, in the direct dehydrogenation of the ethylbenzene produced, some toluene is usually produced with the styrene so that toluene may be removed even at the later stage, such as when separating undehydrogenated ethylbenzene admixed with styrene in the styrene production. Generally, when operating the toluene column within the preferred limits above stated, the C_8+ fraction removed from the bottom thereof will not contain more than 1-2% of toluene. Of course, a wider range toluene can be distilled from the toluene column, thereby removing all of the toluene from the C_8+ residue, but it is preferred to operate the toluene column to produce a pure toluene product as described, leaving a few percent of toluene in the C_8 plus bottoms. It is possible, accordingly, in an alternate procedure to pass the C_8+ bottoms, directly from the toluene column by way of line 319 to the superdistillation unit of Fig. 5; and the residual C_8 xylene isomers together with bottoms from that superdistillation, may be returned by way of line 409 as feed to the xylene column 316. That feed contains substantially no ethylbenzene, whereby the column 316 removed only the mixed xylene from the C_9+ hydrocarbon. When operating in this manner the xylene as net overhead product of column 316 passing through line 330, are sent by way of line 331 to mixed xylene storage.

As shown in Fig. 5 the C_8 or C_8+ fraction, respectively obtained either from lines 330 or 319, depending upon whether the feed is after or before distillation in xylene column 316, is sent first through heat exchanger

344 wherein the temperature is raised usually sufficient to volatilize some of the C_8 aromatics at any positive feed pressure established by pump 346 to overcome the head pressure of the column at the selected point of entry. Upon leaving the heat exchanger 344, the raw feed may be passed to any of several points of either of the distillation columns 348 or 358, by way of line 350, such as to the bottom of the column 348 by way of line 354, to a higher intermediate point through line 356, to a still higher point 352 of column 348, or it may be passed to the center or top of the first column 358 of the series, through line 351 or 353.

The superdistillation in total is effected in a plurality of two, three or more columns, shown here as three columns 348, 358 or 360, using more than 150 plates, such as 200 to 400 plates as preferred, and dividing the same into three columns. Each column as shown, will preferably have from 66 to about 134 plates or stages. The vapors passing overhead from column 358 are introduced at the bottom of the intermediate column 348 by way of line 362, and the vapors passing overhead from column 348 are introduced to the bottom of the column 360 by way of line 364. Simultaneously, the liquid collected as bottoms in column 360 is returned to a point near the top of the preceding column 348 by way of line 366, as impelled by pump 368. The liquid bottoms of column 348 is returned to a point near the top of column 358 by way of line 370, as impelled by pump 372. In this manner one continuous distillation is effected as shown in three separate columns, each having from 66 to 134 plates, whereby the net distilling effect is that of a single column having over 150 and preferably over 200 plates.

The overhead vapors leaving still 360 by way of line 374 are passed through a condenser, preferably an air cooled condenser and to a surge drum 378. Any uncondensed vapors are vented by way of line 380 to a heat exchanger 382 to condense more of the vapors, the cooled liquid and vapor mixture being passed through a vent separator 384 to separate uncondensed vapors, the condensate being returned by way of line 386 to the surge drum 378. Accordingly, the surge drum 378 combined with the vapor condensing unit 382, operates as a refluxing condenser to condense vapors for the surge drum and return the same as condensed liquid to the drum 378 in relatively small quantities, whereby the liquified distillate in drum 378 is maintained as liquid, but only slightly below its boiling point. The hot liquid is withdrawn from the drum 378 by pump 388 by way of line 390 and a large portion at least 40 to 1, preferably 60 to 150:1 of the hot liquid is returned to the top of the final distillation column 360 by way of line 392, as reflux, and a portion passes by way of line 394, through cooler 396, and thence to ethylbenzene storage by way of line 398.

The liquid bottoms from the first column 358 are withdrawn through line 400 as impelled by pump 402, and a portion passes by way of line 404 through heat exchanger 344 and, after cooling further in cooler 406, is withdrawn by way of line 408. Another portion of the bottoms of column 358 in line 404 is passed through line 410 and thence into a reboiler 412, and the hot vaporous reboiler mixture is returned to the lower end of still 358 by way of line 414. In operation of this section, the heated charge introduced to a selected point of one of the columns, such as the mid-point of column 348 under pressure of pump 346, after mixture with vapors also introduced to the bottom from line 362 produced by reboiler 412, will produce liquid bottoms in line 370 which is returned to the top of column 358 as reflux. The bottoms of column 358 after being reboiled in boiler 412 are returned to the bottom of column 358 as a vaporous mixture at a temperature sufficient to volatilize ethylbenzene. The liquid at the bottom of column 360 in similar manner is pumped to the top of

column 348 by pump 368. Finally the hot condensed overhead is returned in part to the top of column 360 according to the critical reflux ratio exceeding 40:1.

Where the raw feed enters the system of Fig. 5 by way of line 330 after removal of C_6+ bottoms in column 316, the bottoms product in line 408 consists of mixed xylenes and may be sent to storage as relatively pure xylenes. Where the feed enters through line 319 as the bottoms product of the toluene column 294, then the product in line 408 is returned to the xylene column 316 by way of line 409 to separate pure mixed xylenes as overhead from the C_6+ , which are then sent to storage by way of line 331.

The following examples illustrate the practice of this invention:

Example I.—A naphthenic feed stock is stabilized as described by Fig. 1 to a boiling point range of 156–300° F. The stock has a 10% boiling point of 180° F., a 50% boiling point of 212° F. and a 90% boiling point of 244° F. and produces 50% over at 212° F., the naphtha analyzing 48% paraffins, 42% naphthenes of which 31% boiled above 226° F., and 10% aromatics. It is passed to a first reactor of a series of four containing platinum suspended on a carrier at a temperature of 915° F. and pressure of 430 p.s.i.g. with a hydrogen to hydrocarbon ratio of 7.5 to 1 molar. It was continuously reheated in passage through the series of reactors, each time to the initial temperature of 915° F., the final outlet temperature being 895° F. and the pressure 325 p.s.i.g. It was stabilized in the stabilizer as illustrated in Fig. 2, the top temperature being maintained at 205° F. and the bottom at 415° F. at a pressure of 160 p.s.i.g. The total catalytic dehydrogenation product yield was 87.5% together with 5 weight percent hydrogen gas and 7.5 percent of gas and liquid stabilizer overhead. The product comprised 45% paraffins, 6% naphthene, and 49% aromatics. It was sent to an extractor system illustrated in Fig. 3, operating in a ratio of 12 parts of solvent to 1 part of hydrocarbon feed with a recycle of 0.35 part of recycle consisting of 90 vol. percent C_6 paraffin, 7 vol. percent aromatics, 1 vol. percent C_8 paraffin and 2 vol. percent C_8 paraffin. The solvent composition consisted of 7% water, 73% diethylene glycol and 20% dipropylene glycol by volume. The raffinate composition was 85% paraffin, 9% naphthene and 6% aromatics. The stripped aromatics was washed with water and clay treated at 425° F. It was then distilled in a benzene column having 40 plates operating at a reflux ratio of 7 to 1 to produce benzene having a distillation range of 0.7° C., a freezing point of 5.39° C. and sp. gr. at 60° F. of 0.884. The bottoms of the benzene distillation were distilled in a toluene column having a reflux ratio of 2.7 to 1 to produce toluene having a distillation range of 0.8° C. and sp. gr. at 60° F. of 0.872. The bottoms of the toluene column were sent to a xylene column having 30 plates operating at a reflux ratio of 0.4 to 1 to produce mixed C_8 aromatics having a boiling point range of 6° C. The C_8 aromatics fraction taken overhead analyzed 1.5% toluene, 28.8% ethylbenzene, 16.0% p-xylene, 37.3% m-xylene and 16.4% o-xylene by weight with no analyzable quantity of non-aromatic hydrocarbon boiling in the range of 130–140° F. The C_8 fraction was then sent to a three column still for superdistillation as illustrated in Fig. 5, each column having 130 plates or a total of 390, and distilled at a reflux ratio of 87 to 1. The overhead product consisted of pure ethylbenzene containing 4.5% toluene. That toluene did not need to be removed, but the product was directly useful for styrene production. In a further distillation merely to remove toluene, the residual ethylbenzene recovered was 99.995% pure.

Example II.—A naphthenic feed stock is adjusted to a boiling range of 226–273° F. and analyzed to contain 58% naphthenes, 7% aromatics and 35% paraffins. It

is catalytically dehydrogenated as illustrated in Fig. 2 at an average inlet temperature of 930° F. and a pressure of 445 p.s.i.g. with a hydrogen to hydrocarbon ratio of 8.0 to 1. It was continuously reheated in passage through the series of reactors to the initial temperature and had a final outlet temperature of 905° F. at a pressure of 334 p.s.i.g. The yield was 86%, the balance being light overhead liquid gases and hydrogen. The product comprises 59.5% aromatics, 8% naphthenes and the balance paraffins. The extracted aromatics as illustrated in Fig. 3 after removal of benzene and toluene to form a 5° C. boiling point range C_8 aromatics fraction was superdistilled with a yield of 33% of ethylbenzene having a purity of 99.992% based upon the C_8 aromatics after removal of toluene.

Example III.—The method of Example I was repeated under exactly the same conditions except that the feed stock to the extraction unit consisted of a virgin gasoline fraction obtained from an aromatic base oil having a boiling point range of 140–340° F. The ethylbenzene, obtained in the final superdistillation consisted of 15% of the total C_8 aromatics fed to the still, and after further removal of the toluene, the ethylbenzene had a purity of 99.995%.

Example IV.—The conditions of Example I were repeated using as feed stock a cracked gasoline reacted at 850° F. in two passes over an alumina catalyst. It was fractionated to the same boiling point range as in Example II and extracted, all conditions being the same throughout as in Example I. 13% of the C_8 fraction fed to a superdistillation unit was recovered as ethylbenzene having a purity of 99.990% after further removal of toluene.

Thus, as herein set forth in detail, ethylbenzene may be commercially obtained from aromatized, preferably a catalytically dehydrogenated naphtha having at least 25% naphthene content in the raw feed stock, using a ratio of at least 4 to 12 times the hydrocarbon content of hydrogen to produce an aromatized product containing from 40–60% aromatics. The C_8 aromatic fraction will contain at least 15% of ethylbenzene which can be recovered in a superdistillation applied in a still comprising over 150 plates at a reflux ratio exceeding 40:1, providing the C_8 aromatic feed is substantially free of stable non-aromatic hydrocarbon boiling in the range of 130 to 140° C. Such pure aromatic fraction becomes practically available by extraction wherein the critical non-aromatics boiling in this range are displaced by lower boiling non-aromatics. The high content of ethylbenzene in the C_8 fraction obtained from catalytic dehydrogenation is in itself surprising since neither virgin gasolines or other catalytic naphthas generally contain such high quantities of ethylbenzene among the C_8 aromatics as become available following the specific procedure set forth herein. Thus, while ethylbenzene may be distilled from a xylene mixture therewith from any source in the superdistillation hereof, providing the mixture is first freed of any stable non-aromatic hydrocarbon exceeding 0.3 weight percent thereof, the production of ethylbenzene following the preferred aromatizing procedure hereof forms a raw material which contains unusually large economically recoverable quantities.

Thus, any virgin or catalytic naphtha having an economically recoverable quantity of ethylbenzene may, after removing substantially all of the non-aromatics and forming a mixed C_8 aromatics fraction containing the ethylbenzene, have the ethylbenzene separated by this superdistillation. Similarly, aromatizing procedures other than one using a platinum type catalyst, may be used providing the aromatization is performed upon a highly naphthenic feed stock, whereby to produce substantial quantities of ethylbenzene in the C_8 fraction.

Various modifications will occur to those skilled in the art and accordingly, it is intended that the description

herein given be regarded as illustrative and not limiting except as defined in the claims appending hereto.

We claim:

1. The method of separating ethylbenzene from a mixture with xylene isomers contained in a hydrocarbon mixture which contains other hydrocarbon components comprising first forming of said hydrocarbon mixture a concentrate fraction of said C_8 hydrocarbons from which the stable non-aromatic hydrocarbons boiling in the range of 130 to 140° C. contained in said fraction in quantity greater than 0.3% have been removed, and then superdistilling the ethylbenzene from said fraction in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1.

2. The method of separating ethylbenzene from a mixture with xylene isomers contained in a predominantly C_8 hydrocarbon fraction comprising first removing stable non-aromatic hydrocarbons boiling in the range of 130 to 140° C. contained in said fraction in quantity greater than 0.3% and then superdistilling the ethylbenzene from said C_8 fraction in a distillation column having from about 200 to 400 distillation stages at a reflux ratio in the range of 60-150:1.

3. The method of recovering ethylbenzene contained in a petroleum hydrocarbon naphtha together with other aromatic hydrocarbons, comprising extracting the aromatic hydrocarbon in said naphtha to produce an aromatic extract containing less than 0.3% of stable non-aromatic hydrocarbons therein, distilling said aromatic extract to remove C_6 and C_7 aromatic hydrocarbons and produce a C_8+ fraction containing ethylbenzene and then superdistilling the ethylbenzene from said C_8+ fraction in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1.

4. The method of recovering ethylbenzene contained in a petroleum hydrocarbon naphtha together with other aromatic hydrocarbons comprising extracting said naphtha with a polar solvent having a preferential solubility for aromatic hydrocarbon to form a hydrocarbon solution in said polar solvent in which the aromatic hydrocarbons are predominant, washing said solution with a liquid hydrocarbon having a boiling point range lower than said aromatic hydrocarbon and having a solubility in said solvent greater than the higher boiling non-aromatic hydrocarbon components dissolved in said solvent, thereby displacing said higher boiling non-aromatic hydrocarbons from said solution, separating the aromatic hydrocarbon from other components of said solution by distillation, distilling from said aromatic hydrocarbon mixture a C_8 aromatics fraction having less than 0.3% of stable non-aromatic hydrocarbon therein and then superdistilling said C_8 aromatic fraction to separate ethylbenzene from other C_8 aromatics in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1.

5. The method of producing ethylbenzene comprising catalytically dehydrogenating a petroleum naphtha rich in hydrocarbons having a boiling point in the approximate range of 226-273° F. and comprising at least 25% naphthene hydrocarbon to form a naphtha containing 40 to 60% of aromatics, extracting the aromatic hydrocarbon from said naphtha under conditions to substantially exclude non-aromatic hydrocarbons exceeding 0.3 volume percent thereof, fractionating the aromatic extract to produce a C_8+ fraction and then superdistilling said fraction in a still having at least 150 distillation stages at a reflux ratio exceeding 40:1 to separate a distillate comprising ethylbenzene containing less than 1% of stable hydrocarbon impurity boiling in the range of 130 to 140° C.

6. The method of producing ethylbenzene comprising catalytically dehydrogenating a high naphthene petroleum naphtha boiling in the range of 100-400° F. at a temperature in the range of 890-975° F. and a pressure of 200-500 p.s.i.g. in the presence of 4 to 12 mols of

hydrogen per mol of hydrocarbon to produce a dehydrogenation product containing 40-60% of aromatic hydrocarbon, extracting said naphtha with a polar solvent having a preferential solubility for aromatic hydrocarbon to form a hydrocarbon solution in said polar solvent in which the aromatic hydrocarbons predominate, washing said solution with a liquid hydrocarbon having a boiling point range lower than said aromatic hydrocarbon and having a solubility in said solvent greater than the higher boiling non-aromatic hydrocarbon components dissolved in said solvent, thereby displacing said higher boiling non-aromatic hydrocarbons from said solution, separating the aromatic hydrocarbon from the other components of said solution by distillation, distilling from the aromatic hydrocarbon mixture a C_8+ aromatics fraction having less than 0.3% of stable non-aromatic hydrocarbon therein and then superdistilling said C_8+ aromatic fraction to separate ethylbenzene from other C_8 aromatic hydrocarbons in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1.

7. The method of producing ethylbenzene of styrene grade of purity comprising aromatizing a petroleum naphtha to produce an aromatic conversion product containing at least 20 percent of ethylbenzene in the C_8 aromatic components, extracting the aromatic hydrocarbon from the aromatic conversion product by solvent extraction with a relatively polar solvent in a manner to produce an aromatic extract containing not more than 0.3% of non-aromatic hydrocarbons therein, fractionating the extract to produce a C_8+ fraction and superdistilling said C_8+ fraction in a still comprising over 300 distillation stages at a reflux ratio in the range of 60 to 80:1 to separate an ethylbenzene containing less than 1 percent of stable non-aromatic hydrocarbon impurity boiling in the range of 130 to 140° C.

8. The method of producing ethylbenzene comprising catalytically dehydrogenating petroleum naphtha boiling in the range of 100-400° F. and containing at least 25% of naphthenes boiling in the range of 226-273° F. at a temperature in the range of 910-930° F. and a pressure of 420-460 p.s.i.g. in the presence of 6 to 8 mols of hydrogen per mol of hydrocarbon to produce a dehydrogenation product containing 40-60% aromatics, extracting said naphtha with a polar solvent having a preferential solubility for aromatic hydrocarbon to form a hydrocarbon solution in said polar solvent in which the aromatic hydrocarbons predominate, washing said solution with a liquid hydrocarbon having a boiling point range lower than said aromatic hydrocarbon and having a solubility in said solvent greater than the higher boiling non-aromatic hydrocarbon components dissolved in said solvent, thereby displacing said higher boiling non-aromatic hydrocarbons from said solution, separating the aromatic hydrocarbon from said other components of said solution by distillation, distilling from the aromatic hydrocarbon mixture a C_8+ aromatics fraction having less than 0.3% of stable non-aromatic hydrocarbon therein and then superdistilling said C_8+ aromatic fraction to separate ethylbenzene from other C_8 aromatics in a distillation column having from 200 to 400 distillation stages at a reflux ratio in the range of 60-150:1.

9. The method of producing ethylbenzene and other aromatic hydrocarbons in a high degree of purity, comprising catalytically dehydrogenating a petroleum naphtha rich in C_6 - C_8 components and containing at least 25 volume percent of naphthenes, to produce a dehydrogenated naphtha comprising 40-60 volume percent of aromatic hydrocarbons, extracting the aromatic hydrocarbon from dehydrogenated naphtha with a polar solvent while displacing non-aromatic hydrocarbons boiling in the range of 130 to 140° C. from said aromatic extract, separating substantially pure benzene from the aromatic extract by fractionally distilling the extract in a column having at least 12 stages at a minimum reflux ratio of 1.35:1, separating substantially pure toluene by fraction-

ally distilling the residue of the benzene distillation in a column of at least 14 stages at a minimum reflux ratio of 1.0:1, separating a C_8 fraction from the residue of the toluene distillation, and superdistilling the C_8 fraction in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1 to separate ethylbenzene containing less than 1% of non-aromatic hydrocarbon boiling in the range of 130 to 140° C.

10. The method of recovering ethylbenzene contained in a petroleum hydrocarbon naphtha together with other aromatic hydrocarbons comprising extracting said naphtha with a polar solvent having a preferential solubility for aromatic hydrocarbon to form a hydrocarbon solution in said polar solvent in which the aromatic hydrocarbons predominate, washing said solution with a liquid hydrocarbon having a boiling point range lower than said aromatic hydrocarbon and having a solubility in said solvent greater than the higher boiling non-aromatic hydrocarbon components dissolved in said solvent, thereby displacing said higher boiling non-aromatic hydrocarbons from said solution, separating the aromatic hydrocarbon from other components of said solution to produce a mixture of aromatic hydrocarbons containing less than 0.3% of non-aromatic hydrocarbon components, distilling said aromatic hydrocarbon in a first preliminary distillation in a distillation column having from about 35 to 45 stages at a reflux ratio in the range of about 5-7:1 to separate therefrom substantially pure benzene, distilling the residue in a second preliminary distillation in a distillation column having from about 35 to 45 distillation stages at a reflux ratio in the range of about 2-4:1 to separate substantially pure toluene, and superdistilling the C_8 + residue in a column having at least 150 distillation stages at a minimum reflux ratio of 40:1 to separate ethylbenzene containing less than 1% of stable hydrocarbon impurity boiling in the range of 130 to 140° C.

11. The method of recovering ethylbenzene contained in a petroleum hydrocarbon naphtha together with other aromatic hydrocarbons comprising extracting said naphtha with a polar solvent having a preferential solubility for aromatic hydrocarbon to form a hydrocarbon solution in said polar solvent in which the aromatic hydrocarbons predominate, washing said solution with a liquid hydrocarbon having a boiling point range lower than said aromatic hydrocarbon and having a solubility in said solvent greater than the higher boiling non-aromatic hydrocarbon components dissolved in said solvent, thereby displacing said higher boiling non-aromatic hydrocarbons from said solution, separating the aromatic hydrocarbon from other components of said solution to produce a mixture of aromatic hydrocarbons containing less than 0.3% of non-aromatic hydrocarbon components, distilling said aromatic hydrocarbon in a first preliminary distillation in a distillation column having from about 35 to 45 stages at a reflux ratio in the range of about 5-7:1 to separate therefrom substantially pure benzene, distilling the residue in a second preliminary distillation in a distillation column having from about 35 to 45 distillation stages at a reflux ratio in the range of about 2-4:1 to separate substantially pure toluene, distilling the C_8 + residue in a third preliminary distillation in a column having from 25 to 35 distillation stages at a reflux ratio of about 0.3 to 0.5:1 to separate a C_8 fraction having a boiling point range of about 4 to 10° C., and superdistilling said C_8 fraction in a column having from 200 to 400 distillation stages at a reflux ratio of 60-150:1 to separate a distillate ethylbenzene containing less than 1% of stable hydrocarbon impurity boiling in the range of 130 to 140° C.

12. Method of recovering ethylbenzene contained in a hydrocarbon naphtha including other aromatic hydrocarbons as well as non-aromatic hydrocarbons comprising extracting said naphtha at a temperature in the range of 220-325° F. at a pressure of 80 to 135 p.s.i.g. with a polar solvent comprising a lower alkylene glycol ether

by continuously passing said solvent under said extracting conditions countercurrently in contact with said naphtha in a ratio of 5 to 30 parts of solvent per part of naphtha by volume to produce an aromatics rich extract solution and aromatics poor raffinate, washing said extract solution with liquid C_8 paraffin hydrocarbon whereby higher boiling non-aromatic hydrocarbon components dissolved in said solvent are displaced from said extract solution into said raffinate while being replaced by said C_8 paraffin hydrocarbon, reducing the pressure of said extract solution to flash off dissolved C_8 hydrocarbon components, stripping the aromatic hydrocarbon from the solvent with steam to separate a fraction comprising substantially 100% aromatic hydrocarbon, distilling from said aromatic hydrocarbon mixture a C_8 + aromatics fraction having less than 0.3% of stable non-aromatic hydrocarbons therein boiling in the range of 130-140° C. and then superdistilling said C_8 + aromatic fraction to separate ethylbenzene in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1.

13. The method of distilling ethylbenzene from a mixture with xylene isomers, said mixture being substantially free of non-aromatic hydrocarbon, comprising passing vapors of the said mixture through distillation columns comprising 150 to 400 distillation stages while washing said vapors with condensed liquid in each stage passing countercurrently from stage to stage as reflux, said 150 to 400 stages being separated into a plurality of two to three distillation columns of from 50 to 134 stages each, by passing the liquid mixture to be distilled to an intermediate stage of said 150 to 400 stages, pumping hot condensed liquid from the bottom of the last column to the top of the preceding column through the series of columns as reflux, pumping a portion of the liquid from the bottom of the first column to a reboiler and returning the same as hot vapors to a point near the bottom of the first column, condensing ethylbenzene vapors from the last column to a hot liquid at about its boiling point and returning a portion of the final hot liquid ethylbenzene condensate to the top of the last column as reflux, said columns being operated at a reflux ratio in the range of about 40 to 150:1.

14. Method of recovering ethyl benzene contained in a petroleum hydrocarbon naphtha together with other aromatic hydrocarbons comprising solvent extracting the aromatic hydrocarbons in said naphtha with a polar solvent to produce an aromatic extract containing less than 0.3% of stable non-aromatic hydrocarbons therein, removing a substantial quantity of other C_6 - C_8 aromatic hydrocarbon components of said extract to produce a C_8 fraction in which ethyl benzene is relatively concentrated, and superdistilling said concentrated ethyl benzene extract in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1 to produce substantially pure ethyl benzene.

15. Method of recovering ethyl benzene contained in a petroleum hydrocarbon naphtha together with other aromatic hydrocarbons comprising solvent extracting the aromatic hydrocarbons in said naphtha with a polar solvent to produce an aromatic extract containing less than 0.3% of stable non-aromatic hydrocarbons therein, distilling said aromatic extract to remove C_6 and C_7 aromatic hydrocarbons therein and produce a C_8 + fraction containing said ethyl benzene removing a portion of the other aromatic components of said C_8 + fraction to produce a C_8 fraction in which the ethyl benzene is relatively concentrated and superdistilling the ethyl benzene from said concentrated C_8 fraction in a distillation column having at least 150 distillation stages at a reflux ratio exceeding 40:1.

References Cited in the file of this patent

UNITED STATES PATENTS

1,955,246 Link ----- Apr. 17, 1934
(Other references on following page)

23

UNITED STATES PATENTS

2,295,256	Brugna	Sept. 8, 1942
2,407,820	Durum	Sept. 17, 1946
2,734,930	Schlatter	Feb. 14, 1956
2,770,663	Grote	Nov. 13, 1956
2,773,918	Stephens	Dec. 11, 1956

FOREIGN PATENTS

625,570	Great Britain	June 30, 1949
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24

OTHER REFERENCES

Rossini et al.: Petroleum Refiner, volume 21, No. 11, November 1942, pages 73-78.
Rossini et al.: Hydrocarbons from Petroleum (1953), Reinhold Publishing Corporation, 330 West 42nd Street, New York, New York, page 342.



US006841714B2

(12) **United States Patent**
Leflaive et al.

(10) **Patent No.:** US 6,841,714 B2
(45) **Date of Patent:** Jan. 11, 2005

(54) **PROCESS FOR CO-PRODUCTION OF
PARAXYLENE, METAXYLENE AND/OR
ORTHOXYLENE**

FOREIGN PATENT DOCUMENTS

WO 99 64381 12/1999

* cited by examiner

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(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 286 days.

(57) **ABSTRACT**

A process for co-production of paraxylene, metaxylene and/or orthoxylene from a hydrocarbon feedstock (1) that comprises [1] a separation stage of the feedstock in a simulated moving bed in a chromatographic column (9) that contains a number of beds of an adsorbent, interconnected in a loop, is described, whereby said column comprises an injection (3) of the feedstock, a draw-off (10) of an extract that consists of paraxylene and desorbent, an intermediate fraction (11) (extract or raffinate) that contains ethylbenzene, and a raffinate (12) that contains a mixture of metaxylene and orthoxylene that is virtually free of ethylbenzene and paraxylene and [2] a crystallization stage (27) of the metaxylene and/or orthoxylene fraction. Upstream from the adsorption zone and/or upstream from the crystallization zone, it is possible to distill the entering mixture to produce an orthoxylene-enriched fraction at the bottom and a metaxylene-enriched fraction at the top.

(21) **Appl. No.:** 10/247,830

(22) **Filed:** Sep. 20, 2002

(65) **Prior Publication Data**

US 2003/0069461 A1 Apr. 10, 2003

(30) **Foreign Application Priority Data**

Sep. 20, 2001 (FR) 01 12177

(51) **Int. Cl.**⁷ C07C 7/12

(52) **U.S. Cl.** 585/828; 585/822; 585/825;
585/812

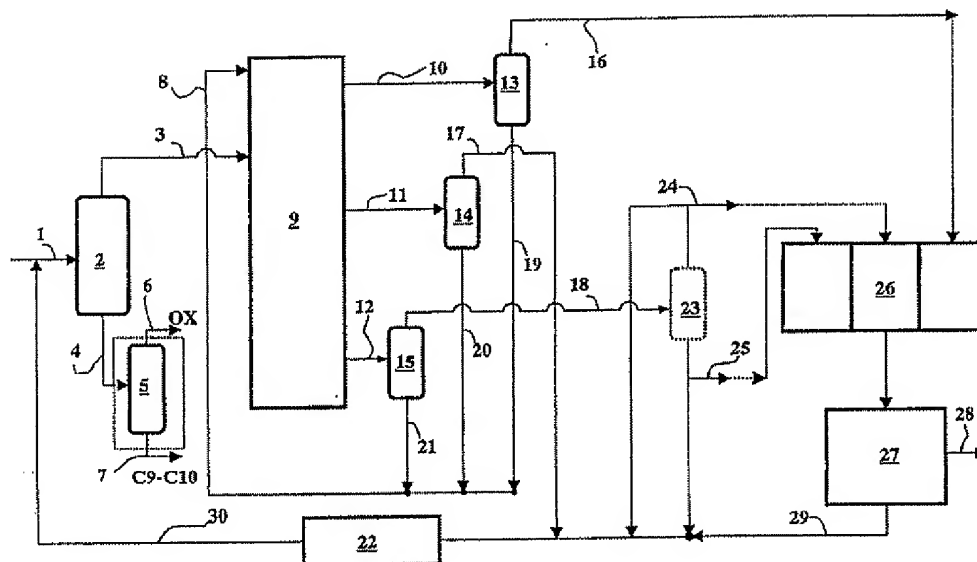
(58) **Field of Search** 585/828, 822,
585/825, 812

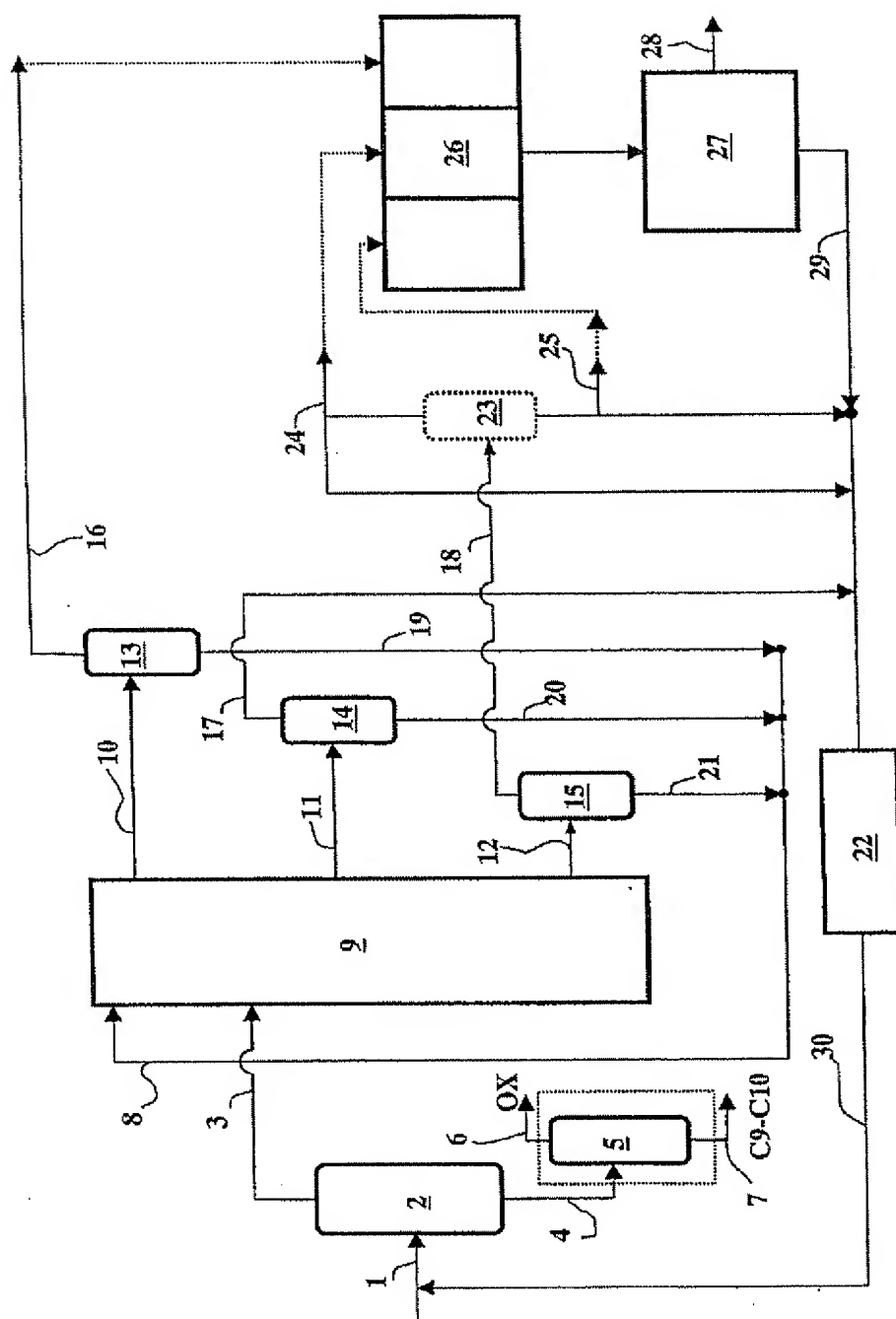
(56) **References Cited**

U.S. PATENT DOCUMENTS

5,284,992 A * 2/1994 Hotier et al. 585/805

20 Claims, 1 Drawing Sheet





PROCESS FOR CO-PRODUCTION OF PARAXYLENE, METAXYLENE AND/OR ORTHOXYLENE

The invention relates to a process for co-production of paraxylene and metaxylene and/or orthoxylene that comprises in combination a simulated moving-bed adsorption unit and a crystallization zone.

The production of high-purity paraxylene by separation by adsorption is well known from the prior art. This market is extensively developed: its outlets are the productions of terephthalic acid, phthalic anhydride and polyethylene terephthalate resins. The technological background that describes the production of paraxylene with very high purity is illustrated in Patent EP-A-531191 of the applicant.

In contrast, the metaxylene market is still restricted, whereby its outlet is isophthalic acid. The separation of metaxylene and obtaining it at a purity level in accordance with market specifications (>99%) is the subject, however, of several processes. Thus metaxylene purification approaches from a C8 aromatic hydrocarbon feedstock have been stipulated in the prior art. Liquid-liquid extraction processes are presented in particular in U.S. Pat. Nos. 2,528,892, 2,738,372, 2,848,517, 2,848,518, 3,309,414, 3,515,768 and 3,584,068. These processes rest on stability criteria of the complex formed by bromine trifluoride (BF₃) and hydrofluoric acid (HF) and xylene isomers, whereby the complex that is formed with the metaxylene is the most stable. The drawback of these techniques is essentially environmental but also financial. Actually, the corrosivity and the danger associated with these products are detrimental and lead to additional costs in terms of equipment.

Other techniques for purification of metaxylene by extraction use different products but result in the same drawbacks. U.S. Pat. Nos. 2,830,105, 3,707,577, 2,562,068 thus teach respectively an extraction with phosphorus pentafluoride and hydrofluoric acid, with lithium chloride and aluminum chloride, and with sulfur dioxide and pentane.

It is also conceivable to purify metaxylene by a selective reaction followed by a separation, by halogenation as described in U.S. Pat. Nos. 2,889,382 and 3,644,552, by sulfonation (U.S. Pat. No. 2,511,711), and even by alkylation (U.S. Pat. No. 3,539,650). These processes are often expensive and involve undesirable additional products.

The extractive distillation processes, shown in U.S. Pat. No. 2,763,604 (extractive distillation with benzonitrile), U.S. Pat. No. 3,089,829 (benzoic acid) and U.S. Pat. No. 3,849,261 (organometallic compounds) exhibit a risk of contaminating products and produce considerable additional costs.

Processes for separating metaxylene by adsorption are presented in U.S. Pat. No. 4,326,092, U.S. Pat. No. 5,382,747, U.S. Pat. No. 5,900,523, which use as adsorbent a sodium-exchanged Y zeolite or a sodium- and lithium-exchanged Y zeolite and which use as desorbents indane or toluene. U.S. Pat. No. 6,137,024 describes a process for separating metaxylene from a mixture that contains the three xylenes (plus optionally ethylbenzene and/or C9 and C10 aromatic compounds) by contact with an H β zeolite. This process can use a desorbent that is preferably benzene, toluene or a combination of these two compounds.

Another method for purifying metaxylene is the use of the crystallization technology without tying it to a separation by adsorption. Such techniques that combine crystallization units in a series are described in U.S. Pat. No. 2,884,470 and U.S. Pat. No. 2,777,888. These processes are based on a preferential crystallization that makes it possible to avoid the problems linked to the eutectic.

A variant of this approach is the process that is disclosed in U.S. Pat. No. 3,277,200, where the co-crystallization of metaxylene and paraxylene is followed by a selective melting of paraxylene crystals to separate them from metaxylene.

The scope of this process, however, is restricted to feedstocks that enter the crystallization stage containing at most 3% ethylbenzene and at most 3% orthoxylene. In U.S. Pat. No. 3,544,646, the co-crystallization of metaxylene and paraxylene is followed by a separation between the metaxylene and the paraxylene based on the density of the crystals. The proximity of the densities (respectively 1.030 g/ml and 1.006 g/ml), however, leads to doubts on the practical implementation of this operation in a commercial optical system. A similar patent, U.S. Pat. No. 3,825,614, presents a co-crystallization followed by a separation by crystal density, but the feedstock that enters this stage is substantially freed of orthoxylene thanks to an upstream orthoxylene distillation (splitter). The orthoxylene is then sent to an isomerization unit.

It now becomes advantageous to co-produce paraxylene and metaxylene in the same complex for production of aromatic compounds. Actually, it recently became evident that the addition of small amounts of polyethylene isophthalate to polyethylene terephthalate improved the properties of the latter. The market requirements call for a larger amount of paraxylene than that of metaxylene: typically 2 to 40 times larger, the paraxylene should be very pure, typically at least 99.7%, and the metaxylene should have reasonable purity, typically at least 99.0%.

The prior art also describes processes of co-production of paraxylene and metaxylene. For example, U.S. Pat. No. 4,368,347 uses a vapor phase process with intermediate fraction recycling: in addition to the complication that is linked to recycling intermediate fractions, this document does not describe and does not suggest how it is possible to use in a practical way such a process that operates at a pressure of between 1 and 2 bar and at a temperature of 150° C. to 200° C. with a feedstock whose bubble point is 145° C. and with fixed beds that have pressure drops of at least 0.1 bar and probably more to operate economically. Patent FR 2 651 148 uses two different solvents to separate the C8-aromatic fraction into three effluents, which greatly limits its scope since the distillations that result from the simulated moving bed separation unit are multiplied. Patent WO 93/22022 describes various cases of separations of feedstocks of three components into three effluents, however the technology that is used that involves very high pressures, pressure regulation and flow rate regulation at the same time in each of the three or four zones of the process and beds that are each separated in a column is justified economically only for products of very high added value.

U.S. Pat. No. 4,306,107 describes a simulated moving-bed process in liquid phase where the metaxylene is sampled in the form of extract; the paraxylene, orthoxylene and a fraction of ethylbenzene are sampled as an intermediate raffinate; and finally the ethylbenzene is sampled as a raffinate. This process that allows the co-production of metaxylene and ethylbenzene naturally does not allow a majority of paraxylene and an accompanying stream of metaxylene to be co-produced.

U.S. Pat. No. 4,313,015 describes a process for continuous co-production of paraxylene and metaxylene from a hydrocarbon feedstock in a simulated moving bed in liquid phase that comprises three samplings. The extract consists of paraxylene that is too impure (99.44%) to be marketed at current standards (current standard=99.7% minimum) and with a yield of 97.5%; the intermediate raffinate consists of

ethylbenzene, orthoxylene, metaxylene and a little paraxylene; finally the raffinate consists primarily of a mixture of orthoxylene and metaxylene. Virtually pure metaxylene is then obtained by distillation of the raffinate.

A process for co-production of paraxylene and metaxylene from a hydrocarbon feedstock in a simulated moving bed in liquid phase that comprises three samplings is also described in Patent FR 2 782 714. The chromatographic column that is described contains at least twenty-five beds that are distributed in five zones. At least five beds should be located in zone 3B that is between the point for draw-off of an intermediate raffinate that contains metaxylene, orthoxylene, ethylbenzene, solvent and paraxylene, and the point for draw-off of a raffinate that contains metaxylene, orthoxylene and solvent. Metaxylene with a purity that is higher than 99% is then obtained by distillation of the raffinate. In addition to the large number of beds necessary for the implementation of the process (30, for example), the hydrocarbon feedstock should have an ethylbenzene content that is less than 5%, which is restricting.

The applicant filed a patent application FR 00/05 424 that describes a process for coproduction in a simulated moving bed of paraxylene and metaxylene in a chromatographic column comprising three samplings from a non-limited feedstock of ethylbenzene where an extract that contains paraxylene is drawn off continuously, a first raffinate is drawn off continuously or intermittently, and where a second raffinate that comprises orthoxylene and metaxylene is drawn off intermittently, whereby the process is also characterized in that the second raffinate is distilled so as to recover pure orthoxylene and metaxylene.

Document U.S. Pat. No. 5,510,562 also describes a process for separation of C8 aromatic compounds where the mixture of orthoxylene, metaxylene, paraxylene and ethylbenzene is first divided into two flows that respectively contain paraxylene and ethylbenzene, and metaxylene and orthoxylene. The paraxylene is then separated from the ethylbenzene by a distillation followed by a crystallization, and the metaxylene is separated from the orthoxylene by distillation.

U.S. Pat. No. 3,700,744 describes a process for the production of paraxylene (PX), orthoxylene (OX), and metaxylene (MX) from a flow of C8 aromatic compounds by first carrying out a fractionated distillation to produce a top fraction that contains ethylbenzene (EB), PX and MX that is lacking in any OX, an intermediate fraction that contains a mixture of PX and MX, and a bottom fraction that contains essentially pure orthoxylene. The top fraction is next isomerized and then recycled in the fractionation zone. The intermediate fraction that contains the PX and the MX is sent into a separation zone by adsorption to produce essentially pure paraxylene and metaxylene. A variant of this process consists in producing paraxylene (PX), orthoxylene (OX) and metaxylene (MX) from a flow of C8 aromatic compounds by first carrying out a distillation to produce a top fraction that contains ethylbenzene (EB), PX and MX and OX, and a bottom fraction that contains a mixture of three xylenes that are lacking in EB. The top fraction is next isomerized and then recycled in the fractionation zone. The bottom fraction that contains the PX and the MX is sent into a zone for separation by adsorption to produce essentially pure paraxylene or metaxylene in an extract and a raffinate that contains a mixture of orthoxylene and the least well-retained compound of paraxylene or metaxylene. The raffinate is then distilled to produce essentially pure metaxylene and orthoxylene.

In all of the processes that are described in U.S. Pat. No. 4,313,015, FR 2 782 714, U.S. Pat. No. 5,510,562 and U.S.

Pat. No. 3,700,744 as well as in Patent Application FR 00/05 424, high-purity metaxylene (>99%) is obtained by distillation. The boiling points of these two compounds, however, are very close (i.e., respectively 139.12° C. and 144.41° C.), which makes it very difficult to obtain high-purity metaxylene by distillation and requires a large column with at least 150 to 200 plates and a very high reflux rate, typically a reflux to feedstock ratio that is higher than 5 to 1. In addition, if the metaxylene and orthoxylene mixture flow that it is sought to separate contains impurities in the form of paraxylene and ethylbenzene, these impurities will be concentrated in the metaxylene, making it difficult to obtain a purity that is higher than 99.0%.

In Example E, U.S. Pat. No. 5,900,523 describes a process for the production of xylenes where a first zone for separation by paraselective adsorption produces a paraxylene-enriched extract and a raffinate that comprises at least the majority of orthoxylene and metaxylene that are present in the feed flow and that contains more than 10 percent of orthoxylene. The extract is distilled to recover high-purity paraxylene. The raffinate of the first separation zone is then introduced into a second separation zone by metaselective adsorption where the adsorbent is a Y zeolite with an SiO₂/Al₂O₃ molar ratio of between 4.0 and 6.0 that is exchanged with sodium and that has a water content that is equivalent to a fire loss at 500° C. from about 1.5 to about 2.5% by weight; the separation is conducted in a liquid phase at a temperature of between 100° C. and 150° C. The second zone of separation by metaselective adsorption produces a metaxylene-enriched extract and a raffinate that comprises the non-adsorbed compounds of the first raffinate, in particular orthoxylene. High-purity metaxylene is recovered from the extract.

The two patents that are closest to this invention are U.S. Pat. No. 3,773,846 and WO 99/64381. U.S. Pat. No. 3,773, 846 as well as the patents described below thus propose the linking of a paraxylene production unit and purification of metaxylene by adsorption or crystallization, and optionally an isomerization unit. U.S. Pat. No. 3,798,282 and U.S. Pat. No. 3,825,614 present metaxylene crystallization methods downstream from a paraxylene crystallization unit. The crystallization techniques that are used allow a coarse separation of metaxylene crystals that are larger than the paraxylene crystals. After this first separation, the concentrated metaxylene can be melted and recrystallized in a second stage to produce high-purity metaxylene. U.S. Pat. No. 3,773,846 shows the advantage of an adsorption stage prior to the crystallization to reduce the paraxylene concentration in the metaxylene crystallization unit. It claims a simultaneous production process of high-purity metaxylene and high-purity paraxylene from a fresh feedstock of C8 aromatic hydrocarbons. The first zone is a selective adsorption zone that produces a high-purity paraxylene flow and a paraxylene-depleted flow at a concentration that is below the eutectic binary metaxylene-paraxylene. A fractionation stage of this depleted flow makes it possible to produce at the top a mixture of metaxylene and orthoxylene, whereby the latter is in a proportion smaller than that of the eutectic mixture. This mixture is introduced into a crystallization unit that makes it possible to produce a high-purity metaxylene flow and a mother liquor. The fractions that are collected at the bottom of the fractionation column and the mother liquor of the crystallization are recycled in an isomerization zone to produce a mixture of C8 aromatic hydrocarbons in conditions close to the thermodynamic equilibrium. The fresh feedstock can be introduced directly into the selective adsorption zone or into the isomerization zone before the adsorption stage.

Likewise, Patent WO 99/64381 uses the crystallization as a metaxylene separation technique. The first stage for separation of paraxylene and metaxylene from the feedstock of C8 aromatic compounds is done by simulated moving-bed adsorption after the feedstock passes into a distillation column that produces at the bottom an orthoxylene-rich flow and a distillate that contains for the most part ethylbenzene, paraxylene and metaxylene. As a result, the composition of the mixture and in particular the paraxylene content is modified by the adsorption stage, which affects the crystallization and induces a different design of crystallization units. The crystallization stage exhibits several variants, structured around successive crystallizations below the eutectic point, with or without a crystallization drum. This patent proposes several methods for separating orthoxylene and uses a transalkylation unit rather than an isomerization unit to isomerize the recycled orthoxylene.

A common point in U.S. Pat. No. 3,773,846 and WO 99/64381 is the presence of ethylbenzene in the raffinate that is drawn off from the adsorption unit. U.S. Pat. No. 3,773, 846, moreover, notes this drawback by proposing a distillation that makes it possible to deplete of ethylbenzene the flow that enters into the crystallization unit. In Patent WO 99/64381, the ethylbenzene is sent directly into the crystallization unit, which needlessly increases the entering flow.

This invention has as its object to eliminate the above-mentioned drawbacks.

The object of the invention is the co-production of paraxylene and metaxylene and/or orthoxylene that can be marketed from a hydrocarbon feedstock. The main object of the invention is to obtain paraxylene with a purity of at least 99.7%. The second object of the invention is to produce about 10 to 15 times less metaxylene than paraxylene but with a purity that is at least equal to 99% and/or orthoxylene with a purity that is at least equal to 98.5%.

More specifically, the invention relates to a process for co-production of paraxylene and metaxylene and/or orthoxylene from a feedstock that contains xylenes, ethylbenzene and C9-C10 hydrocarbons, whereby the process successively comprises:

A passage of feedstock (1) in a column for distillation of xylenes (2) from where a mixture (3) that comprises the majority of metaxylene, paraxylene, ethylbenzene and at least a portion of orthoxylene is drawn off at the top, and from where a flow (4) of C9-C10 hydrocarbons and the remaining portion of orthoxylene is drawn off at the bottom;

A separation of top mixture (3) in a simulated moving bed in at least one chromatographic column (9) containing a number of beds of an adsorbent that are interconnected in a closed loop and having a different selectivity for paraxylene, ethylbenzene, metaxylene and orthoxylene, whereby said column comprises at least five zones that are delimited by injections of mixture (3) (adsorption feedstock) and a desorbent (8) and draw-offs of an extract (10) that contains paraxylene, an intermediate fraction (11) that contains ethylbenzene, a raffinate (R2) (12) that contains orthoxylene and metaxylene, whereby a paraxylene desorption zone 1 is included between the injection of the desorbent and the sampling of the extract, whereby a zone 2 for desorption of ethylbenzene, orthoxylene and metaxylene is included between the sampling of the extract and the injection of the adsorption feedstock, whereby a zone 3A for paraxylene adsorption is included between the injection of the feedstock and the draw-off of the intermediate fraction, whereby a zone 3B for ethylben-

zene adsorption is included between the draw-off of the intermediate fraction and the draw-off of raffinate (R2), and whereby a zone 4 is included between the draw-off of raffinate (R2) and the injection of desorbent, whereby the process is characterized in that:

Raffinate (2) is distilled to eliminate essentially all of the desorbent, and a distilled raffinate (18) is drawn off,

The extract is distilled to recover a paraxylene-enriched fraction (16).

The process is also characterized in that:

Either distilled raffinate (18) is sent at least in part to at least one crystallization zone (27), and metaxylene with a purity of at least 99% is recovered,

Or distilled raffinate (18) is sent at least in part into a second distillation zone (23), a top flow (24) that contains metaxylene and a bottom fraction (25) that contains orthoxylene are recovered, the top flow is crystallized at least in part, metaxylene with a purity of at least 99% is recovered, and/or said bottom fraction is crystallized at least in part, and orthoxylene with a purity of at least 98.5% is recovered.

The stage for separation of paraxylene and metaxylene is done by a simulated moving-bed adsorption from where are drawn off an extract that comprises paraxylene and desorbent, an intermediate fraction (extract or raffinate) that contains ethylbenzene with a strong yield, and a raffinate that contains a mixture of metaxylene and orthoxylene that is virtually free of ethylbenzene and paraxylene. The draw-off of an ethylbenzene-rich intermediate fraction makes the presence of ethylbenzene splitter superfluous. Actually, the feedstock that enters the crystallization zone is virtually free of ethylbenzene, which makes possible the reduction of the entering flow and an optimized operation of the unit.

The crystallization of the metaxylene and/or orthoxylene fraction can be carried out in one or more stages and is in general conducted so as to obtain a preferred final purity of at least 99.0%, whereby the yield of metaxylene or orthoxylene relative to the feedstock can be adapted to a value of 3 to 30%.

On the other hand, it is possible to choose a unit that typically comprises 24 beds in the case, for example, of a unit revamping. Preferably, in the case of a new unit, the configuration can use 26 or 28 beds.

The chromatographic column that operates in simulated countercurrent or in simulated co-current can preferably comprise at least 24 beds and at least three beds in zone 3B.

The feedstock can have a content of linear and branched alkanes and naphthenes that is less than 1% by weight and advantageously a naphthene content that is less than 0.3%. The feedstock in general contains less than 10% by weight of ethylbenzene. It can come from either a unit for transalkylation of C7 and C9 into xylenes or from a unit for catalytic dismutation of toluene into benzene and xylenes, or from a unit for isomerization of a fluid that contains ethylbenzene, whereby said unit can be operated in the presence of a catalyst that dealkylates ethylbenzene into benzene as described in U.S. Pat. No. 5,516,656 and WO 98/05 613.

During the first simulated moving-bed separation stage, the intermediate fraction and raffinate (R2) can be drawn off continuously or intermittently. By drawing off the raffinate preferably continuously, it is possible to inject it continuously in the desorbent distillation stage, without an intermediate buffer tank.

According to a characteristic of the process, it is possible to initiate the purification by crystallization of the extract

from which desorbent was previously removed by distillation. This crystallization will preferably be conducted between +10° C. and -30° C. as described in, for example, Patent EP 531 191-B1. The mother liquor that is obtained from the crystallization can then be recycled at the feed of the simulated moving-bed chromatography. The solvent for washing paraxylene crystals that are obtained is selected, for example, from among the following solvents: n-pentane, water, purified paraxylene or toluene, and the washing liquor that results from the washing stage can be recycled in the feed of the adsorption column in a simulated moving bed.

According to a characteristic of the process, mixture (4) of orthoxylene and C9-C10 aromatic hydrocarbons drawn off at the bottom of distillation column (2) can be sent into another distillation column (5), from where a high-purity (at least 98.5%) orthoxylene flow (6) is extracted at the top, and a flow (7) that contains C9-C10 hydrocarbons is extracted at the bottom. Flow (3) that is drawn off at the top of the distillation column that is placed upstream from the adsorption unit usually contains less than 5% by weight of orthoxylene. While the amount of orthoxylene that enters the first stage for separation of paraxylene by adsorption is considerably lower, its content in raffinate (R2) is reduced, and the metaxylene crystallization yield is thereby improved.

According to one of two variants for the process, raffinate (R2) from which the desorbent is removed can be sent at least in part to a second distillation column (23) from where an orthoxylene-enriched flow (25) is drawn off at the bottom, and a metaxylene-enriched flow (24) that feeds crystallization zone (27) is drawn off at the top. In the case where little or no orthoxylene is desired to be produced, this distillation is thus localized advantageously between the simulated moving-bed unit and the crystallization zone. A partial distillation is then sufficient to obtain at the top of the column a feedstock with a sufficient metaxylene content so that the crystallization zone operates with a correct yield. The crystallization stage will make it possible to limit the number of plates and avoid high reflux and reboiling rates, contrary to U.S. Pat. No. 4,313,015, FR 2 782 714 and U.S. Pat. No. 5,510,562 where the purification of the metaxylene requires a large column with at least about 150 to 200 plates.

According to a characteristic of the invention, at least a portion of the orthoxylene-enriched flow that exits from second column (25) can be isomerized in at least one isomerization zone, and the isomerate that is obtained is recycled in distillation column (2).

According to another characteristic of the process, the adsorbent that is used in the first separation stage can comprise an X zeolite that is exchanged with barium or a Y zeolite that is exchanged with potassium or a Y zeolite that is exchanged with barium and potassium.

The preferred desorbent is paradiethylbenzene, however other desorbents such as toluene, paradifluorobenzene or diethylbenzenes in a mixture can also be suitable.

According to another characteristic of the invention, the volumetric ratio of desorbent to feedstock in the first separation stage can be between 0.5 and 2.5, preferably between 1.4 and 1.7.

According to another characteristic of the invention, it is possible to carry out the first stage of the process at a temperature that is generally between 20° C. and 250° C., preferably between 90° C. and 210° C., and more particularly between 160° C. and 200° C. and under a pressure that is between the bubble pressure of xylenes at the operating temperature and 20 bar (1 bar=0.1 MPa).

According to a preferred characteristic of the invention, for the production of metaxylene, it is possible to regulate

the flow rates of zones 3A and 3B as well as the optional distillation of orthoxylene in column (2) and/or second column (23) to obtain as a crystallization feedstock an effluent that is virtually free of ethylbenzene and desorbent and a molar composition that is delimited by the four points: pure metaxylene, eutectic binary metaxylene-paraxylene (metaxylene 87.0%, paraxylene 13.0%), eutectic ternary meta-ortho-paraxylene (metaxylene 61.4%, orthoxylene 30.5%, paraxylene 8.1%), and eutectic binary meta-ortho-xylene (metaxylene 66%, orthoxylene 33.4%).

According to an embodiment of the process, line (24) that is drawn off at the top of the column and line (25) that is drawn off at the bottom of column (23) are generally connected at the inlet of one or more crystallization batch vat(s) (26). Line (16) of paraxylene with a purity of at least 99.7% can also feed, in a restricted amount, a crystallization batch vat so as to obtain paraxylene of very high purity. The objective of using these batch vats is to make it possible for each to produce isomers in runs, by obtaining, after passage in crystallization zone (27), a purified flow (28) that comprises either metaxylene with at least 99.0%, or orthoxylene with at least 98.5%, or ultra-pure paraxylene with at least 99.90% and, for example, greater than 99.95%.

According to a variant embodiment, the crystallization of metaxylene and that of orthoxylene can be carried out in a single crystallization zone, in runs, to produce metaxylene and orthoxylene separately.

According to another variant, the crystallization of the metaxylene and that of orthoxylene can be carried out in different crystallization zones.

For the production of orthoxylene by crystallization, it is possible to regulate the flow rates of zones 3A and 3B, as well as the optional distillation of orthoxylene in column (2) and/or column (23) to obtain as crystallization feedstock an effluent that is essentially free of ethylbenzene and desorbent and a molar composition that is delimited by the four points: pure orthoxylene, eutectic binary orthoxylene-paraxylene (orthoxylene 75.7%, paraxylene 24.3%), eutectic ternary meta-ortho-paraxylene (metaxylene 61.4%, orthoxylene 30.5%, paraxylene 8.1%), and eutectic binary meta-ortho-xylene (metaxylene 66.6%, orthoxylene 33.4%).

According to a preferred characteristic of the invention, the crystallization zones can consist of one or more crystallizers, for example static crystallizers that alternate between a cooling phase and a heating phase. A refrigeration unit is used to operate at a temperature of between -45° C. and -60° C. in the case where it is sought to produce metaxylene, between -20° C. and -60° C. in the case where it is sought to produce orthoxylene, and between 20° C. and -50° C. in the case where it is sought to produce paraxylene. After obtaining the desired fraction (metaxylene, orthoxylene or paraxylene), the remaining mother liquor is drawn off from the crystallizer. The purest crystalline layer continues to adhere to the static crystallizer plates. These crystals are then purified by initiating heating at a temperature that is slightly higher than the crystallization point. This partial melting and this resuspension wash the crystals and make it possible to obtain a product with a purity that is greater than 99% and greater than 99.90% for the ultra-pure paraxylene. Washing with said high-purity product or a combination of washing and a partial melting are other alternatives for the purification of crystals. Separated mother liquor (29) can then be recycled continuously in isomerization unit (22).

In the case where it is sought to produce metaxylene in the crystallization zone, it will be possible to use this known method of the prior art for the separation of metaxylene by

crystallization. It is possible to cite, for example, the Sulzer Chemtec processes that are described in the journal Chemical Engineering, May 2000, and in Patents WO 99/64381 and U.S. Pat. No. 3,773,846.

According to another characteristic according to which the chromatographic column produces paraxylene, not at at least 99% purity with a low productivity, but at at least 50% purity with a high productivity, it is possible to send the thus produced fraction from which desorbent is removed into at least one crystallization zone to deliver paraxylene crystals and a mother liquor; the crystals are separated from the mother liquor, optionally resuspended, washed and recovered; and the mother liquor can be recycled at least in part in the chromatographic column.

The crystallization and the various stages of separation of the mother liquor and paraxylene purification are described in, for example, U.S. Pat. No. 6,147,272 and U.S. Pat. No. 6,111,161 of the applicant.

The crystals that are formed can be washed by suitable washing solvents; the very high-purity product is recovered, and the washing liquor that results therefrom that comprises the impurities can be recycled in the resuspension zone.

The productivity of the adsorption unit is thereby maximized by releasing purity constraints on the paraxylene that is obtained from the adsorption unit and by ensuring the final purity of this product by at least one crystallization stage. This purity can reach at least 99.6% and preferably at least 99.7%, whereby the purity of metaxylene and/or that of orthoxylene remain unchanged, however.

Furthermore, the operating costs of the adsorption unit are minimized because it is possible to operate it with a small number of beds and a low level of solvent. It is actually possible to work preferably with at most 24 beds and even more particularly with 20 beds. It is also possible to minimize the amount of desorbent by injecting it into zone 1 and by injecting the feedstock into zone 3A of the column in a volumetric ratio of desorbent to feedstock of at most 1.7:1, for example in a ratio of between 0.7 and 1.5, and very advantageously between 1.2 and 1.5.

The invention will be better understood based on FIG. 1 that illustrates the co-production of paraxylene and metaxylene and/or orthoxylene continuously or intermittently in a simulated moving bed and in countercurrent, combined with a crystallization zone.

A feedstock of xylenes comprising metaxylene, orthoxylene, ethylbenzene and paraxylene is introduced continuously via a line (1) into a column (2) for distillation of xylenes from where a flow (3) that comprises metaxylene, orthoxylene, ethylbenzene and paraxylene is drawn off at the top, and a flow (4) that consists of C₉-C₁₀ compounds and a portion of orthoxylene is drawn off at the bottom. Flow (4) can be distilled in a distillation column (5) that delivers essentially pure orthoxylene at the top via a line (6) and C₉-C₁₀ hydrocarbons at the bottom via a line (7). Flow (3) is introduced continuously into at least one chromatographic column (9) with at least five zones that contain a number of beds, 24 beds for example, of an adsorbent that comprises a zeolite, an X zeolite that is exchanged with barium, for example, and that operates in a liquid phase in a simulated moving bed and in counter-current according to U.S. Pat. No. 4,313,015 and the already cited patent of the applicant. An intermediate fraction (R1) is drawn off continuously via a line (11) at a point that is located downstream from the point of introduction of the feedstock, while a raffinate (R2) that contains metaxylene and orthoxylene is drawn off continuously via a line (12) downstream from the intermediate raffinate relative to the direction of flow of fluids in the

column (specifically from the bottom to the top). A desorbent, paradiethylbenzene, is injected continuously via a line (8) at a point of the column that is located upstream from the injection point of the feedstock while an extract that contains desorbent and essentially pure paraxylene is drawn off continuously via a line (10) at a point that is located downstream from the injection point of the desorbent. This extract is distilled in a distillation column (13), from which an essentially pure paraxylene (greater than 99.7%) is drawn off at the top via a line (16), and the desorbent that can be recycled in the chromatographic column is drawn off at the bottom via a line (19).

Intermediate fraction (R1) is introduced into a distillation column (14) from which the desorbent that can be recycled is drawn off at the bottom via a line (20), and a mixture that contains xylenes and ethylbenzene is drawn off at the top via a line (17) that makes it possible to send it to an isomerization unit (22).

Raffinate (R2) is introduced into a distillation column (15) from which the desorbent that can be recycled in line (8) is drawn off at the bottom via a line (21), and a mixture that contains essentially metaxylene and orthoxylene and that is virtually free of paraxylene and ethylbenzene is drawn off at the top via a line (18). This line (18) is connected to the inlet of a column for distillation of orthoxylene (23) from where a metaxylene-enriched flow (24) is drawn off at the top, and an orthoxylene-enriched flow (25) is drawn off at the bottom. Flows (24) and (25) can be recycled in an isomerization unit (22) or sent to a crystallization zone (27). The pure crystals are separated from a mother liquor and recovered via a line (28). The mother liquor that is obtained from the crystallization is sent via a line (29) into isomerization unit (22).

The isomerate that is obtained is recycled via a line (30) into line (1) for feed of the feedstock of distillation column (2).

The invention is illustrated by the following examples that are given as non-limiting.

EXAMPLE 1

The production of paraxylene from a feedstock from which hydrocarbons comprising 9 and 10 carbon atoms were previously removed and that comprises a mixture of xylenes and ethylbenzene with the following composition by weight:

EB: Ethylbenzene 5.6%

PX: Paraxylene 22.6%

MX: Metaxylene 49.9%

OX: Orthoxylene 21.9%

is carried out in a simulated moving bed in counter-current.

The pilot unit that is used to do this consists of 24 columns that are 1.1 m in length and 0.021 m in diameter. 344 g of barium-exchanged X zeolite with a moisture level of 5.5%, expressed in terms of fire loss at 900° C., is loaded per column. The operating temperature is 175° C., the pressure at the intake of the recycling pump is kept at 10 bar, all of the flows are injected or drawn off continuously with the flow rate being monitored, with the exception of the intermediate raffinate that is drawn off continuously with the pressure being monitored, and the injection and draw-off flow rates are expressed in ambient conditions of pressure and at 20° C. A raffinate (R2) and an intermediate fraction R1 (intermediate raffinate) are drawn off continuously. The total number of beds is 24. Five beds are counted between the injection of desorbent and the draw-off of raffinate, 9 beds between the draw-off of extract and the injection of feedstock, 5 beds between the injection of feedstock and the

draw-off of intermediate raffinate, 3 beds between the draw-off of intermediate raffinate and the draw-off of raffinate and 2 beds between the draw-off of raffinate and the injection of desorbent.

The operating conditions are as follows:

Feedstock: 3.24 l.h^{-1}
Solvent: 5.52 l.h^{-1} of desorbent (99.06% of paradiethylbenzene and 0.94% of other C_{10} aromatic hydrocarbons)

Extract: 3.27 l.h^{-1}

Intermediate raffinate (R1): 4.29 l.h^{-1}

Raffinate (R2): 1.2 l.h^{-1}

Recycling flow rate (in zone 1): 16.4 l.h^{-1}

The R2/R1 ratio is 0.28.

The switching time of the valves (or period) is 70.8 seconds.

After the paradiethylbenzene is distilled, the extract that is obtained that is drawn off continuously delivers a flow of 0.71 l/h of paraxylene with 99.7% purity.

The 1.2 l.h^{-1} of raffinate is distilled, and a fluid flow rate of 0.13 l.h^{-1} is obtained whose composition by weight is as follows:

EB: Ethylbenzene 0.1%

PX: Paraxylene 1.7%

MX: Metaxylene 73.9%

OX: Orthoxylene 24.2%

The crystallization zone comprises two static crystallizers that alternate between a cooling phase and a heating phase when the crystals are produced. A refrigeration unit is used to produce metaxylene crystals at -60°C . After crystallization, the mother liquor is drawn off. The metaxylene crystals are washed with very high-purity molten metaxylene and are simultaneously purified by a partial melting at -45°C .

The metaxylene yield of the crystallization is 29%.

The amount of paraxylene that is produced by the overall unit is 25 times greater than the amount of metaxylene, or respectively 0.71 l/h of paraxylene with 99.7% purity and 0.028 l/h of metaxylene with 99.0% purity.

EXAMPLE 2

Example 1 is repeated by adding a column for distillation of the orthoxylene before the crystallization zone to improve the crystallization yield.

As above, the 1.2 l.h^{-1} of raffinate R2 is distilled, and a fluid flow rate of 0.13 l.h^{-1} is obtained whose composition by weight is as follows:

EB: Ethylbenzene 0.1%

PX: Paraxylene 1.7%

MX: Metaxylene 73.9%

OX: Orthoxylene 24.2%

The metaxylene yield is 6%. Raffinate 2 that is free of desorbent is then sent into an orthoxylene distillation column. A fluid flow rate of 0.05 l/h is drawn off at the bottom of the column, and the composition of this fluid by weight is as follows:

PX: Paraxylene 1.2%

MX: Metaxylene 49.4%

OX: Orthoxylene 49.4%

The orthoxylene yield at the bottom of the column is 79%.

At the top of the column, the fluid that is drawn off at a rate of 0.08 l/h has a composition by weight as follows:

EB: Ethylbenzene 0.2%

PX: Paraxylene 2.1%

MX: Metaxylene 89.4%

OX: Orthoxylene 8.3%.

The flow rates that relate to the input of the distillation (splitter) and the crystallization are 1 and 0.61. The metaxylene yield of the crystallization that is produced according to that of Example 1 is 72%.

The amount of paraxylene that is produced by the global unit is 13.7 times greater than the amount of metaxylene, or respectively 0.71 l/h of paraxylene with 99.7% purity and 0.05 l/h of metaxylene with 99.0% purity.

EXAMPLE 3

The same operating conditions as in Example 2 are repeated, but the ratio of the raffinate flow rates (R2) and intermediate raffinate (R1):R2/R1 is modified. The flow rates are as follows:

Feedstock: 3.24 l.h^{-1}

Solvent: 5.52 l.h^{-1} of desorbent (99.06% of paradiethylbenzene and 0.94% of other C_{10} aromatic hydrocarbons)

Extract: 3.27 l.h^{-1}

Intermediate raffinate (R1): 3.45 l.h^{-1}

Raffinate (R2): 2.04 l.h^{-1}

Recycling flow rate (in zone 1): 16.4 l.h^{-1}

Ratio R2/R1 is 0.59.

The switching time of the valves (or period) is 70.8 seconds.

After paradiethylbenzene is distilled, the extract that is obtained and that is drawn off continuously delivers a flow of 0.71 l/h of paraxylene with 99.7% purity.

The 2.04 l.h^{-1} of raffinate R2 is distilled, and a fluid flow rate of 0.39 l.h^{-1} is obtained whose composition by weight is as follows:

EB: Ethylbenzene 0.07%

PX: Paraxylene 0.98%

MX: Metaxylene 69.8%

OX: Orthoxylene 29.1%

The metaxylene yield is 17%. Raffinate R2 is then sent into an orthoxylene distillation column. A fluid flow rate of 0.17 l/h is drawn off at the bottom of the column, and the composition by weight of the fluid is as follows:

PX: Paraxylene 0.8%

MX: Metaxylene 59.0%

OX: Orthoxylene 40.2%

The orthoxylene yield at the bottom of the column is 60%.

At the top of the column, the fluid that is drawn off at a rate of 0.22 l/h has the following composition by weight:

EB: Ethylbenzene 0.1%

PX: Paraxylene 1.1%

MX: Metaxylene 78.2%

OX: Orthoxylene 20.6%.

The flow rates that relate to the input of the splitter and the crystallization are 1 and 0.56. The metaxylene yield of the crystallization according to that of Example 1 is 41.5%.

The amount of paraxylene that is produced by the overall unit is 9.75 times greater than the amount of metaxylene, or respectively 0.71 l/h of paraxylene with 99.7% purity and 0.072 l/h of metaxylene with 99.0% purity.

EXAMPLE 4

This example illustrates the production of paraxylene from a feedstock from which C_9 and C_{10} hydrocarbons are essentially removed and that comprises a mixture of xylenes

and ethylbenzene that is more concentrated in ethylbenzene than in the preceding examples and that has the following composition by weight:

EB: Ethylbenzene 8.5%

PX: Paraxylene 21.1%

MX: Metaxylene 48.9%

OX: Orthoxylene 21.4%.

The separation of paraxylene is carried out in the same pilot unit as the one that is described in Example 1 and that consists of 24 beds that are 1.1 meters in length and 0.021 m in diameter and that contains a barium-exchanged X zeolite. A raffinate (raffinate 2) and an intermediate raffinate are drawn off continuously.

The operating conditions are as follows:

Feedstock: 3.24 l.h^{-1}

Solvent: 5.52 l.h^{-1} of desorbent (99.06% of paradiethylbenzene and 0.94% of other C_{10} aromatic hydrocarbons)

Extract: 3.24 l.h^{-1}

Intermediate raffinate (R1): 4.11 l.h^{-1}

Raffinate (R2): 1.41 l.h^{-1}

Recycling flow rate (in zone 1): 16.4 l.h^{-1}

The configuration is 5 beds, 9 beds, 5 beds, 3 beds and 2 beds respectively in zones 1, 2, 3A, 3B and 4.

The ratio R2/R1 is 0.34.

The switching time of the valves (or period) is 70.8 seconds.

After the paradiethylbenzene is distilled, the extract that is obtained and that is drawn off continuously delivers a flow of 0.66 l/h of paraxylene with 99.7% purity.

The 1.41 l.h^{-1} of raffinate is distilled, and a fluid flow rate of 0.19 l.h^{-1} is obtained whose composition by weight is as follows:

EB: Ethylbenzene 0.2%

PX: Paraxylene 1.4%

MX: Metaxylene 70.2%

OX: Orthoxylene 28.2%

The metaxylene yield is 8.6%. Raffinate 2 is then sent into a distillation column.

At the top of the column, a fluid flow of 0.103 l/h is drawn off whose composition by weight is as follows:

EB: Ethylbenzene 0.34%

PX: Paraxylene 1.8%

MX: Metaxylene 87.1%

OX: Orthoxylene 10.7%.

The flow rates that relate to the input of the distillation column and the crystallization are 1 and 0.55. The metaxylene yield of the crystallization that is carried out according to that of Example 1 is 64%.

The amount of paraxylene that is produced by the overall unit is 11 times greater than the amount of metaxylene, or respectively 0.66 l/h of paraxylene with 99.7% purity and 0.06 l/h of metaxylene with 99.0% purity.

At the bottom of said column, a fluid flow rate of 0.087 l/h is drawn off that can be sent into a crystallization unit at a temperature of -60°C . to produce orthoxylene with 98.5% purity, after a resuspension of orthoxylene crystals at -20°C . and washing by pure orthoxylene.

EXAMPLE 5

In this example, the feedstock of the following composition by weight:

EB: Ethylbenzene 5.6%

PX: Paraxylene 22.6%

MX: Metaxylene 49.9%

OX: Orthoxylene 21.9%

undergoes a first distillation stage before entering the adsorption unit in a simulated moving bed. The feedstock flow rate is 4.98 l/h. The distillation stage has as its object to deplete of orthoxylene the flow that penetrates the adsorption unit. An orthoxylene-enriched flow of 1.94 l/h is drawn off at the bottom of the column. The flow that is drawn off at the bottom of the column is distilled in a second column for distilling xylenes. At the top, a flow rate of a flow that contains pure orthoxylene with 99% purity is recovered. The flow that exits at the top of the first column with a flow rate of 3.04 l/h is depleted of orthoxylene and has the following composition by weight:

EB: Ethylbenzene 6.7%

PX: Paraxylene 28.3%

MX: Metaxylene 60.1%

OX: Orthoxylene 4.9%.

This flow is directed to the adsorption unit. The separation of the paraxylene is carried out in the same pilot unit as the one that is described in Example 1 and that consists of 24 beds that are 1.1 meters in length and 0.021 m in diameter containing a barium-exchanged X zeolite. A raffinate (raffinate 2) and an intermediate raffinate are drawn off continuously. The configuration is 5 beds, 9 beds, 5 beds, 3 beds and 2 beds respectively in zones 1, 2, 3A, 3B and 4.

The operating conditions are as follows:

Entering flow: 3.04 l.h^{-1}

Solvent: 5.17 l.h^{-1} of desorbent (99.06% of paradiethylbenzene and 0.94% of other C_{10} aromatic hydrocarbons)

Extract: 3.03 l.h^{-1}

Intermediate raffinate (R1): 3.98 l.h^{-1}

Raffinate (R2): 1.2 l.h^{-1}

Recycling flow rate (in zone 1): 16.05 l.h^{-1}

The switching time of the valves (or period) is 70.8 seconds.

After paradiethylbenzene is distilled, the extract that is obtained and that is drawn off continuously delivers a flow of 0.83 l/h of paraxylene with 99.7% purity.

The 1.2 l.h^{-1} of raffinate is distilled, and a fluid flow rate of 0.12 l.h^{-1} is obtained whose composition by weight is as follows:

EB: Ethylbenzene 0.1%

PX: Paraxylene 1.9%

MX: Metaxylene 92.3%

OX: Orthoxylene 5.6%.

The metaxylene yield is 6%. The metaxylene yield of the crystallization that is produced according to that of Example 1 is 79%.

The amount of paraxylene that is produced by the overall unit is about 10 times greater than the amount of metaxylene that is produced, or respectively 0.83 l/h of paraxylene with 99.7% purity and 0.086 l/h of metaxylene with 99.0% purity.

EXAMPLE 6

It is desired to produce paraxylene with the strongest productivity possible and simultaneously metaxylene in an amount that is about fifteen times less. The pilot unit that is used to do this consists of 20 columns that are 1.1 m in length and 0.021 m in diameter. 344 g of barium-exchanged X zeolite with a moisture level of 5.5%, expressed in terms of fire loss at 900°C ., is loaded per column. The operating temperature is 175°C ., the pressure at the intake of the recycling pump is kept at 10 bar, all of the injected or

drawn-off flows have the flow rate being monitored, with the exception of the intermediate raffinate that has the pressure being monitored; and the injection and draw-off flow rates are expressed in ambient pressure conditions and at 20° C. Four beds are counted between the injection of desorbent and draw-off of extract, 7 beds between the draw-off of extract and the injection of feedstock, 4 beds between the injection of feedstock and the draw-off of intermediate raffinate, 3 beds between the draw-off of intermediate raffinate and the draw-off of raffinate and 2 beds between the draw-off of raffinate and the injection of desorbent.

63 cm³/min of feedstock with the following composition is injected:

Ethylbenzene 5.54%
Paraxylene 22.59%
Metaxylene 49.9%
Orthoxylene 21.97%.

78.75 cm³/min of desorbent that consists of 98.9% of paradiethylbenzene and 0.7% of metadiethylbenzene are injected, whereby the difference at 100 consists of about ten components of C10 aromatic compounds.

38.5 cm³/min of extract with the following composition by weight is drawn off:

Ethylbenzene 0.098%
Paraxylene 34.75%
Metaxylene 0.655%
Orthoxylene 2.87%

Paradiethylbenzene 63.81%, whereby the difference at 100% consists of C10 aromatic compounds.

79.3 cm³/min of intermediate raffinate is drawn off, whose composition by weight is:

Ethylbenzene 4.35%,
Paraxylene 0.94%,
Metaxylene 35.74%,
Orthoxylene 15.93%,

PDEB 42.73%, whereby the difference at 100% consists of C10 aromatic compounds.

23.95 cm³/min of raffinate R2 is drawn off, whose composition by weight is:

Ethylbenzene 0.2%,
Paraxylene 0.44%,
Metaxylene 11.83%,
Orthoxylene 4.57%,

PDEB 82.68%, whereby the difference at 100% consists of C10 aromatic compounds.

The switching period is 60.7 seconds, and the flow rate of the recycling stream in zone 1 is 295.7 cm³/min expressed at 50° C.

It is noted that in the extract, the purity of paraxylene is 97% for a yield of 94%. By contrast, relative to a market where the paraxylene would be produced with at least 99.6% purity with a yield of 96.6%, the solvent rate was reduced from 1.7 to 1.25, the productivity increased by 40%, and the absolute number of beds was reduced from 24 to 20.

The extract is distilled and sent into crystallization. The paraxylene crystals are separated from the mother liquor by centrifuging, resuspended, washed by molten, pure paraxylene and collected. Starting from paraxylene with 97% purity, paraxylene with a purity of approximately 99.6% will be obtained with 98% yield; for a crystallization temperature of -20°, the paraxylene content of the mother liquor will be about 38%. This mother liquor is recycled at the inlet of the adsorption column with the fresh feedstock.

Likewise, raffinate R2 is first distilled to recover the paradiethylbenzene. At the top of the column to be distilled, a mixture is obtained whose composition by weight is:

Ethylbenzene 0.11%,
Paraxylene 2.59%,
Metaxylene 70.18%,
Orthoxylene 27.12%.

This mixture is partially distilled before the crystallization zone to obtain at the top a metaxylene-enriched composition of the composition by weight:

Ethylbenzene 0.17%,
Paraxylene 3.08%,
Metaxylene 83.48%,
Orthoxylene 13.27%.

This mixture is subjected to a crystallization according to that of Example 1, and pure metaxylene at 99% with a yield of 55% is obtained.

The orthoxylene-enriched bottom fraction is recycled in the isomerization stage.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

The entire disclosure of all applications, patents and publications, cited above and below, and of corresponding French Application No. 01/12.177, filed Sep. 20, 2001 is hereby incorporated by reference.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

What is claimed is:

1. Process for co-production of paraxylene and metaxylene and/or orthoxylene from a feedstock that contains xylenes, ethylbenzene and C9-C10 hydrocarbons, whereby the process successively comprises:

A passage of feedstock (1) in a column (2) for distillation of xylenes from where a mixture (3) that comprises the majority of metaxylene, paraxylene, ethylbenzene and at least a portion of orthoxylene is drawn off at the top, and from where a flow (4) of C9-C10 hydrocarbons and the remaining portion of orthoxylene is drawn off at the bottom;

A separation of top mixture (3) in a simulated moving bed in at least one chromatographic column (9) containing a number of beds of an adsorbent that are interconnected in a closed loop and having a different selectivity for paraxylene, ethylbenzene, metaxylene and orthoxylene, whereby said column comprises at least five zones that are delimited by injections of mixture (3) (adsorption feedstock) and a desorbent (8) and draw-offs of an extract (10) that contains paraxylene, an intermediate fraction (11) that contains ethylbenzene, a raffinate (R2) (12) that contains orthoxylene and metaxylene, whereby a paraxylene desorption zone 1 is included between the injection of the desorbent and the sampling of the extract, whereby a zone 2 for desorption of ethylbenzene, orthoxylene and metaxylene is included between the sampling of the extract and the injection of the adsorption feedstock, whereby a zone 3A for paraxylene adsorption is included between the injection of the feedstock and the draw-off of the intermediate fraction, whereby a zone 3B for ethylben-

zene adsorption is included between the draw-off of the intermediate fraction and the draw-off of raffinate (R2), and whereby a zone 4 is included between the draw-off of raffinate (R2) and the injection of desorbent, whereby the process is characterized in that

Raffinate (2) is distilled to eliminate essentially all of the desorbent, and a distilled raffinate (18) is drawn off,

The extract is distilled to recover a paraxylene-enriched fraction (16).

The process is also characterized in that:

Either distilled raffinate (18) is sent at least in part to at least one crystallization zone (27), and metaxylene with a purity of at least 99% is recovered,

Or distilled raffinate (18) is sent at least in part into a second distillation zone (23), a top flow (24) that contains metaxylene and a bottom fraction (25) that contains orthoxylene (24) are recovered, the top flow is crystallized at least in part, metaxylene with a purity of at least 99% is recovered, and/or said bottom fraction is crystallized at least in part, and orthoxylene with a purity of at least 98.5% is recovered.

2. A process according to claim 1, in which flow (4) is distilled in a distillation column (5) to produce a high-purity orthoxylene flow (6) at the top and a flow (7) that contains C9-C10 hydrocarbons at the bottom.

3. A process according to one of claim 1, in which the crystallization of metaxylene and the crystallization of orthoxylene are carried out in a single crystallization zone, in runs, to produce metaxylene or orthoxylene separately.

4. A process according to one of claim 1, in which the crystallization of metaxylene and the crystallization of orthoxylene are carried out in separate crystallization zones.

5. A process according to one of claim 1, in which a portion of orthoxylene-enriched bottom fraction (25) is isomerized in at least one isomerization zone, and the isomerate that is obtained is recycled in distillation column (2).

6. A process according to one of claims 1, in which the adsorbent that is used in the separation stage is a barium-exchanged X zeolite or a potassium-exchanged Y zeolite or a barium- and potassium-exchanged Y zeolite.

7. A process according to one of claims 1, in which the desorbent is selected from among paradiethylbenzene, toluene, paradifluorobenzene or mixed with diethylbenzenes.

8. A process according to one of claims 1, in which the volumetric ratio of desorbent to adsorption feedstock is between 0.5 and 2.5.

9. A process according to claim 1, in which the separation stage is conducted at a temperature that is generally between 20° C. and 250° C., and under a pressure that is between the bubble pressure of xylenes at the operating temperature and 20 bar.

10. A process according to claim 1, in which to produce high-purity metaxylene, the flow rates of zones 3A and 3B as well as the distillation of orthoxylene in column (2) and/or second column (23) are regulated to obtain as a crystallization feedstock an effluent that is essentially free of ethylbenzene and desorbent, with a molar composition that is delimited by the four points: pure metaxylene, eutectic binary metaxylene-paraxylene (metaxylene 87.0%, paraxylene 13.0%), eutectic ternary meta-ortho-paraxylene (metaxylene 61.4%, orthoxylene 30.5%, paraxylene 8.1%), and eutectic binary meta-ortho-xylene (metaxylene 66.6%, orthoxylene 33.4%).

lene 13.0%), eutectic ternary meta-ortho-paraxylene (metaxylene 61.4%, orthoxylene 30.5%, paraxylene 8.1%), and eutectic binary meta-ortho-xylene (metaxylene 66.6%, orthoxylene 33.4%).

11. A process according to claim 1, in which at least a portion of paraxylene-enriched fraction (16) feeds a crystallization batch vat to obtain, in runs, after passage into crystallization zone (27), a paraxylene flow (28) at at least 99.90%.

12. A process according to claim 1, in which to produce orthoxylene, the flow rates of zones 3A and 3B as well as the distillation of orthoxylene in column (2) and/or second column (23) are regulated to obtain as a crystallization feedstock an effluent that is essentially free of ethylbenzene and desorbent, with a molar composition that is delimited by the four pure orthoxylene points: eutectic binary orthoxylene-paraxylene (orthoxylene 75.7%, paraxylene 24.3%), eutectic ternary meta-ortho-paraxylene (metaxylene 61.4%, orthoxylene 30.5%, paraxylene 8.1%), and eutectic binary meta-ortho-xylene (metaxylene 66.6%, orthoxylene 33.4%).

13. A process according to claim 1, in which the crystallization zone or zones comprise at least one crystallizer and in which a refrigeration unit is used to operate at a temperature of between -45° C. and -60° C. in the case where it is sought to produce metaxylene, between -20° C. and -60° C. in the case where it is sought to produce orthoxylene and between 20° C. and -50° C. in the case where it is sought to produce paraxylene and in which the mother liquor that is separated from the crystals is entrained to a storage vat after the crystallization stage to be recycled in the isomerization unit.

14. A process according to claim 1, in which the chromatographic column contains at least 24 beds, including at least 3 beds in zone 3B.

15. A process according to claim 1, in which fraction (16) is enriched with paraxylene at at least 50% purity and is sent into at least one crystallization zone to deliver paraxylene crystals and a mother liquor, the crystals are separated from the mother liquor, optionally resuspended, washed and recovered, and the mother liquor is recycled in the chromatographic column.

16. A process according to claim 8, wherein said volumetric ratio is between 1.4 and 1.7.

17. A process according to claim 9, wherein said temperature is between 90° C. and 210° C.

18. A process according to claim 9, wherein said temperature is between 160° C. and 200° C.

19. A process according to claim 1, wherein distilled raffinate (18) is sent at least in part to at least one crystallization zone (27), and metaxylene with a purity of at least 99% is recovered.

20. A process according to claim 1, wherein distilled raffinate (18) is sent at least in part into a second distillation zone (23), a top flow (24) that contains metaxylene and a bottom fraction (25) that contains orthoxylene (24) that contains metaxylene and a bottom fraction (25) that contains orthoxylene (24) are recovered, the top flow is crystallized at least in part, metaxylene with a purity of at least 99% is recovered, and/or said bottom fraction is crystallized at least in part, and orthoxylene with a purity of at least 98.5% is recovered.

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Ind. Eng. Chem. Res., **39** (5), 1228-1234, 2000. 10.1021/ie990426q S0888-5885(99)00426-1

Web Release Date: March 28, 2000

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Dehydrogenation of Ethylbenzene with Carbon Dioxide Using Activated Carbon-Supported Catalysts

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Received for review June 15, 1999

Revised manuscript received December 1, 1999

Accepted February 9, 2000

Abstract:

Dehydrogenation of ethylbenzene to styrene under excess carbon dioxide flow was carried out over activated carbon-supported metal oxide catalysts (Cr, Mn, Co, Ni, Mo, Ru, La, and Ce) at 823 K and *W/F* = 35 g of catalyst-h/mol. The highest yield of styrene (about 40%) with selectivity of above 80% was obtained using activated carbon-supported chromium oxide (Cr/AC) and cerium oxide (Ce/AC) catalysts. The initial activities of the Cr/AC and Ce/AC catalysts were comparable to that of an iron-loaded activated carbon catalyst reported previously. Only chromium(III) oxide and cerium(IV) oxide were detected by X-ray diffraction before and after reactions at higher loading levels, and these species might have been active forms. However, a reduced chromium oxide species was detected by X-ray photoelectron spectroscopy after reaction under argon. In addition to the produced styrene, equivalent amounts of carbon monoxide and water were formed. These results suggest that the dehydrogenation of ethylbenzene to styrene proceeds via two reaction paths. One is the simple dehydrogenation and an oxidation reaction of hydrogen formed with carbon dioxide. The other is the oxidative dehydrogenation of ethylbenzene through the redox cycle of chromium(III) oxide.

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